

APPENDIX K

**STATISTICAL AND GEOCHEMICAL EVALUATION
OF METALS DATA**

STATISTICAL

Statistical Comparison of Site and Background Data For Range J, Parcel 202(7) Fort McClellan, Alabama

1.0 Introduction

This report provides the Tier 1 and Tier 2 site-to-background comparison results for Range J, Parcel 202(7), Fort McClellan, in Calhoun County, Alabama. Tier 1 and Tier 2 evaluations (Shaw E & I, 2003) have been performed on the surface soil, total soil (surface soil and subsurface soil combined), and groundwater data sets. In the first step of the comparison, the maximum detected concentration (MDC) of each element is compared to two times the arithmetic mean of the background data (SAIC, 1998). Any metal that has an MDC greater than the background screening value is carried forward for Tier 2 evaluation, which includes the Slippage Test, the Wilcoxon Rank Sum Test (WRS), and Hot Measurement Test.

The methodology and results of the Tier 1 and Tier 2 comparisons are summarized in Tables 1 through 3, and described in more detail in the following sections. Site samples used in the site-to-background comparison include eight surface soil samples (0 to 1 foot below ground surface [bgs]), 16 total soil samples (1 to 3 feet bgs), and one groundwater sample, that were collected at the site.

Background distributions and screening values have been established for target analyte list metals in surface soil (0 to 1 foot bgs), combine surface and subsurface soil (0 to 12 feet bgs), and groundwater for Fort McClellan (SAIC, 1998).

2.0 Comparison Methodology

This section describes the statistical techniques that were employed in the Range J site-to-background comparisons.

2.1 Statistical Procedures

Contamination can be caused by a variety of processes that yield different spatial distributions of elevated contaminant concentrations. Slight but pervasive contamination can occur from non-point-source releases, and can result in slight increases in contaminant concentrations in a large percentage of samples. Localized, or “hot-spot,” contamination can result in elevated concentrations in a small percentage of the total number of site samples. No single two-sample statistical comparison test is sensitive to both of these modes of contamination. For this reason, the use of several simultaneous tests is recommended for a valid and complete comparison of site

Table 1

**Summary of Site to Background Comparison
Surface Soil, Range J, Parcel 202(7)
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	hits above bkgr max	Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	8 / 8	Passed	0	NA	NA	NA	
Antimony	8 / 8	Passed	0	NA	NA	NA	
Arsenic	8 / 8	Failed	0	Passed	Failed	NA	Yes
Barium	8 / 8	Passed	0	NA	NA	NA	
Beryllium	8 / 8	Passed	0	NA	NA	NA	
Cadmium	0 / 8	NA	NA	NA	NA	NA	
Calcium	8 / 8	Failed	0	Passed	Failed	NA	Yes
Chromium	8 / 8	Failed	0	Passed	Failed	NA	Yes
Cobalt	8 / 8	Passed	0	NA	NA	NA	
Copper	8 / 8	Failed	1	Passed	Failed	NA	Yes
Iron	8 / 8	Failed	0	Passed	Failed	NA	Yes
Lead	8 / 8	Passed	0	NA	NA	NA	
Magnesium	8 / 8	Failed	0	Passed	Passed	NA	
Manganese	8 / 8	Passed	0	NA	NA	NA	
Mercury	8 / 8	Failed	0	Passed	NA ^e	Passed	
Nickel	8 / 8	Failed	0	Passed	Failed	NA	Yes
Potassium	8 / 8	Passed	0	NA	NA	NA	
Selenium	0 / 8	NA	NA	NA	NA	NA	
Silver	0 / 8	NA	NA	NA	NA	NA	
Sodium	0 / 8	NA	NA	NA	NA	NA	
Thallium	0 / 8	NA	NA	NA	NA	NA	
Vanadium	8 / 8	Failed	0	Passed	Failed	NA	Yes
Zinc	8 / 8	Failed	0	Passed	Failed	NA	Yes

NA = not applicable; MDC = maximum detected concentration; UTL = upper tolerance limit

^a Tier 1 evaluation (site MDC compared to 2 x the background mean) per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

^b Part of Tier 2 evaluation per the above referenced memo.

^c Performed only when the Slippage test and/or WRS test cannot be performed.

^d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

^e WRS test is not performed on data sets containing 50% or more nondetects.

Table 2

**Summary of Site to Background Comparison
Total Soil, Range J, Parcel 202(7)
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	hits above bkgrd max	Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	16 / 16	Passed	0	NA	NA	NA	
Antimony	16 / 16	Passed	0	NA	NA	NA	
Arsenic	16 / 16	Failed	1	Passed	Failed	NA	Yes
Barium	16 / 16	Passed	0	NA	NA	NA	
Beryllium	16 / 16	Failed	1	Passed	Failed	NA	Yes
Cadmium	0 / 16	NA	NA	NA	NA	NA	
Calcium	15 / 16	Failed	0	Passed	Passed	NA	
Chromium	16 / 16	Failed	0	Passed	Failed	NA	Yes
Cobalt	16 / 16	Failed	0	Passed	Failed	NA	Yes
Copper	16 / 16	Failed	1	Passed	Failed	NA	Yes
Iron	16 / 16	Failed	1	Passed	Failed	NA	Yes
Lead	16 / 16	Passed	0	NA	NA	NA	
Magnesium	16 / 16	Failed	0	Passed	Passed	NA	
Manganese	16 / 16	Passed	0	NA	NA	NA	
Mercury	16 / 16	Failed	0	Passed	NA ^e	Failed	Yes
Nickel	16 / 16	Failed	1	Passed	Failed	NA	Yes
Potassium	16 / 16	Passed	0	NA	NA	NA	
Selenium	0 / 16	NA	NA	NA	NA	NA	
Silver	0 / 16	NA	NA	NA	NA	NA	
Sodium	0 / 16	NA	NA	NA	NA	NA	
Thallium	0 / 16	NA	NA	NA	NA	NA	
Vanadium	16 / 16	Failed	0	Passed	Failed	NA	Yes
Zinc	16 / 16	Failed	2	Passed	Failed	NA	Yes

NA = not applicable; MDC = maximum detected concentration; UTL = upper tolerance limit

^aTier 1 evaluation (site MDC compared to 2 x the background mean) per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

^b Part of Tier 2 evaluation per the above referenced memo.

^c Performed only when the Slippage test and/or WRS test cannot be performed.

^d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

^e WRS test is not performed on data sets containing 50% or more nondetects.

Table 3

**Summary of Site to Background Comparison
Groundwater, Range J, Parcel 202(7)
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	hits above bkgr max	Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	19 / 30	Failed	0	Passed	Passed	NA	
Antimony	0 / 30	NA	NA	NA	NA	NA	
Arsenic	3 / 30	Passed	NA	NA	NA	NA	
Barium	30 / 30	Passed	NA	NA	NA	NA	
Beryllium	0 / 30	NA	NA	NA	NA	NA	
Cadmium	0 / 30	NA	NA	NA	NA	NA	
Calcium	30 / 30	Failed	0	Passed	Passed	NA	
Chromium	3 / 30	Failed	0	Passed	NA ^d	Passed	
Cobalt	0 / 30	NA	NA	NA	NA	NA	
Copper	0 / 30	NA	NA	NA	NA	NA	
Iron	21 / 30	Passed	NA	NA	NA	NA	
Lead	1 / 30	Passed	NA	NA	NA	NA	
Magnesium	30 / 30	Failed	0	Passed	Failed	NA	Yes
Manganese	25 / 30	Passed	NA	NA	NA	NA	
Mercury	0 / 30	NA	NA	NA	NA	NA	
Nickel	1 / 30	Failed	0	Passed	NA ^d	Passed	
Potassium	13 / 30	Failed	2	Passed	NA ^d	Failed	Yes
Selenium	3 / 30	Failed	0	Passed	NA ^d	Passed	
Silver	0 / 30	NA	NA	NA	NA	NA	
Sodium	30 / 30	Failed	0	Passed	Passed	NA	
Thallium	0 / 30	NA	NA	NA	NA	NA	
Vanadium	1 / 30	Passed	NA	NA	NA	NA	
Zinc	9 / 30	Passed	NA	NA	NA	NA	

NA = not applicable; MDC = maximum detected concentration; UTL = upper tolerance limit

^a Tier 1 evaluation (site MDC compared to 2 x the background mean) per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

^b Part of Tier 2 evaluation per the above referenced memo.

^c Performed only when the Slippage test and/or WRS test cannot be performed.

^d WRS test is not performed on data sets with greater than 50% nondetects.

versus background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 2002).

Analytes that fail the Tier 1 and Tier 2 comparisons are subject to a geochemical evaluation to determine if the elevated concentrations are due to natural processes or if they represent potential contamination.

2.1.1 Tier 1 - In this step of the background screening process, the maximum detected concentration (MDC) of the site data set is compared to the background screening value of two times the background mean (SAIC, 1998). Elements for which the site MDC does not exceed the background screening value are considered to be present at background concentrations, and are not considered site-related chemicals. Elements for which the site MDC exceeds the background screening value undergo further evaluation (Tier 2).

2.1.2 Tier 2 –

Slippage Test – The nonparametric Slippage test is designed to detect a difference between the upper tails of two distributions, and has been recommended for use in site-to-background comparisons to identify potential localized, or hot-spot, contamination (U.S. Navy, 2002). The test is performed by counting the number (K) of detected concentrations in the site data set that exceed the maximum background measurement, and then comparing this number to a critical value (K_c), which is a function of the number of background samples and the number of site samples. If $K > K_c$, then potential contamination is indicated and the analyte will be subjected to geochemical evaluation. If $K \leq K_c$, then localized contamination is not suspected.

Critical values tables for site and background data sets up to size $n = 50$ are provided in U.S. Navy (2002). Critical values for larger data sets are calculated using the test statistic provided in Rosenbaum (1954). In this report, the Slippage test is performed at the 95 percent confidence level. The test cannot be performed if the maximum background value is a nondetect, because the actual concentration in that sample is unknown.

Wilcoxon Rank Sum Test. The nonparametric WRS test is designed to detect a difference between the medians of two data sets, and has been recommended for use in site-to-background comparisons to identify slight but pervasive contamination (EPA, 2000; U.S. Navy, 2002). In this report, the WRS test is performed when the site and background data sets each contain less than 50 percent nondetects (i.e., measurements reported as not detected below the laboratory reporting limit). The WRS test will not be performed on data sets containing 50 percent or more

nondetects. The medians of such data sets are unknown, and hence the test results would lack sufficient power to yield reliable results.

The WRS test compares two data sets of size n and m ($n > m$), and tests the null hypothesis that the samples were drawn from populations with distributions having the same medians. To perform the test, the two sets of observations are pooled and arranged in order from smallest to largest. Each observation is assigned a rank; that is, the smallest is ranked 1, the next largest is ranked 2, and so on up to the largest observation, which is ranked $(n + m)$. If ties occur between or within samples, each one is assigned the mid-rank. Next, the sum of the ranks of smaller data set m is calculated. Then the test statistic Z is determined,

$$Z = \frac{W - m(m + n + 1)/2}{\sqrt{mn(m + n + 1)/12}}$$

Where:

W = Sum of the ranks of the smaller data set

m = Number of data points in smaller group

n = Number of data points in larger group.

This test statistic Z is used to find the two-sided significance. For instance, if the test statistic yields a probability of a Type I error (p-level) less than 0.2, then there is a statistically significant difference between the medians at the 80 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.2, then there is no reasonable justification to reject the null hypothesis at the 80 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and it can be assumed to be drawn from the same population.

If the p-level is less than 0.2, then the medians of the two distributions are significantly different at the 80 percent confidence level. This can occur if the site data are shifted higher or lower than the background data. If the site data are shifted higher relative to background, then contamination may be indicated, and the analyte in question will be carried on for geochemical evaluation; however, if the site data are shifted lower relative to background, then contamination is not indicated. If the p-level is greater than 0.2, then pervasive site contamination is not suspected.

Box Plots. A quick, robust graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot comparison (EPA, 1989 and 1992). These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50 percent of the data points so that the top of the box represents the 75th percentile and the bottom of the box represents the 25th percentile. The small box within the larger box represents the median of the data set. The upper whisker extends outward from the box to the maximum point and the lower whisker extends to the minimum point. Nondetect results are set equal to one-half of the reporting limit for plotting purposes.

For each analyte, box plots of site and background data are placed side by side to visually compare the distributions and qualitatively determine whether the data sets are similar or distinct. Accordingly, the box plots are a necessary adjunct to the WRS test. As described previously, the WRS test may indicate that the medians of the site and background data sets are significantly different. Examination of the box plots will confirm whether that difference is caused by site data that are shifted higher or lower relative to background.

Hot Measurement Test. The hot measurement test consists of comparing each site measurement with a concentration value that is representative of the upper limit of the background distribution (EPA, 1994). Ideally, a site sample with a concentration above the background screening value would have a low probability of being a member of the background distribution, and may be an indicator of contamination. It is important to select such a background screening value carefully so that the probability of falsely identifying site samples as contaminated or uncontaminated is minimized.

The 95th upper tolerance limit (95th UTL) is recommended as a screening value for normally or lognormally distributed analytes and the 95th percentile is recommended as a screening value for nonparametrically distributed analytes (EPA, 1989, 1992, and 1994). Site samples with concentrations above these values are not necessarily contaminated, but should be considered suspect. To perform the test, each analyte's site MDC is compared to the background 95th UTL or 95th percentile, in accordance with the type of background distribution. If the site MDC exceeds the background screening value, then that analyte will undergo a geochemical evaluation. If the MDC does not exceed the background threshold value, then hot-spot contamination is not indicated.

2.1.3 Geochemical Evaluation

If an analyte fails either of the statistical tests described above then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The methodology and results of the geochemical evaluation are provided separately in this appendix.

3.0 Results of the Site-to-Background Comparisons

This section presents the results of the site-to-background comparisons for 23 TAL metals in the Range J surface soil, total soil, and groundwater samples. The WRS test results with corresponding box plots are provided in Attachment 1. Tables 1 through 3 summarize the Tier 1 and Tier 2 test results for each media as discussed in the following sections.

3.1 Surface Soil

Twenty-three TAL metals were evaluated in the Range J surface soil data set. Cadmium, selenium, silver, sodium, and thallium were not detected in surface soil, so no further discussion of these metals is included. Aluminum, antimony, barium, beryllium, cobalt, lead, manganese and potassium were not detected at concentrations above their respective background screening values, and thus they pass the Tier 1 evaluation. These metals are not discussed further. The remaining eleven metals are carried forward for Tier 2 evaluation.

Table 1 summarizes the surface soil statistical site to background comparison results. Box plots are provided in Attachment 1.

Arsenic

Tier 1 Evaluation

Three site samples exceed the background screening value of 13.73 mg/kg.

Slippage Test

K_c for arsenic is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, arsenic passes the Slippage test.

WRS Test

The p-level of 0.002 indicates significant difference between the site and background distributions.

Box Plot

The site minimum, 25th percentile, median, 75th percentile, and interquartile range are higher than the corresponding background values. The site maximum is lower than the corresponding background values (Figure 1-1).

Conclusion

Because arsenic in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Calcium

Tier 1 Evaluation

Two site samples exceed the background screening value of 1,723 mg/kg.

Slippage Test

K_c for calcium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$ calcium passes the Slippage test.

WRS Test

The p-level of 0.059 indicates a significant difference between the site and background distributions.

Box Plots

The site minimum, median, 25th percentile, and 75th percentile are higher than the corresponding background values; however, the site maximum is lower than the corresponding background value (Figure 1-2).

Conclusion

Because calcium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Chromium

Tier 1 Evaluation

Two site samples exceed the background screening value of 37.04 mg/kg.

Slippage Test

K_c for chromium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, chromium passes the Slippage test.

WRS Test

The p-level of 0.008 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, 75th percentile and interquartile range are higher than the respective background values; however, the site maximum is lower than the respective background value (Figure 1-3).

Conclusion

Because chromium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Copper

Tier 1 Evaluation

Three site samples exceed the background screening value of 12.71 mg/kg.

Slippage Test

K_c for copper is 2, and one site sample exceed the maximum background measurement ($K=1$). Because $K < K_c$, copper passes the Slippage test.

WRS Test

The p-level of 0.018 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, and 75th percentile are higher than the respective background values; however, the site maximum is similar to the respective background value (Figure 1-4).

Conclusion

Because copper in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Iron

Tier 1 Evaluation

One site sample exceeds the background screening value of 34,154 mg/kg.

Slippage Test

K_c for iron is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$ iron passes the Slippage test.

WRS Test

The p-level of 0.103 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and median are higher with respect to the corresponding background values. The site interquartile range is within the background interquartile range. The site maximum is lower than the corresponding background value (Figure 1-5).

Conclusion

Because iron in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Magnesium

Tier 1 Evaluation

One site sample exceeds the background screening value of 1,033 mg/kg.

Slippage Test

K_c for magnesium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, magnesium passes the Slippage test.

WRS Test

The p-level of 1 indicates no difference between the site and background distributions.

Box Plot

The site minimum is higher than the corresponding background value. The site maximum is lower than the corresponding background value, the site median is similar to the corresponding background values, and the site interquartile range is within the background interquartile range (Figure 1-6).

Conclusion

Magnesium in surface soil is considered within the range of background.

Mercury

Tier 1 Evaluation

One site sample exceeds the background screening value of 0.08 mg/kg.

Slippage Test

K_c is 2, and no site samples exceed the maximum background measurement ($K=0$). Since $K < K_c$, mercury passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

Box Plot

The site minimum, median, 25th percentile, and 75th percentile are elevated relative to their corresponding background values (Figure 1-7). The shape and location of the background box plot reflects the high percentage of nondetects (60 percent), and the replacement values of one-half the reporting limit rather than detected concentrations. Also, the site maximum is lower than the corresponding background value.

Hot Measurement Test

No site samples exceed the background 95th percentile of 0.125 mg/kg.

Conclusion

Mercury in surface soil is considered within the range of background.

Nickel

Tier 1 Evaluation

One site sample exceeds the background screening value of 10.33 mg/kg.

Slippage Test

K_c for nickel is 2, and no site samples exceed maximum background measurement ($K=0$). Because $K < K_c$ nickel passes the Slippage test.

WRS Test

The p-level of 0.192 indicates a difference between the site and background distributions.

Box Plot

The site minimum is higher than the corresponding background values; however, the site maximum is lower than the corresponding background value, and the site median is similar to its corresponding background value. The site interquartile range is within background interquartile range. (Figure 1-8).

Conclusion

Because nickel in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Vanadium

Tier 1 Evaluation

One site sample exceeds the background screening value of 58.84 mg/kg.

Slippage Test

K_c for vanadium is 2, no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, vanadium passes the Slippage test.

WRS Test

The p-level of 0.018 indicates a significant difference between the site and background distributions.

Box Plots

The site minimum, median, 25th percentile, and 75th percentile are higher than the corresponding background values; however, the site maximum is lower than the corresponding background value (Figure 1-9).

Conclusion

Because vanadium in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Zinc

Tier 1 Evaluation

Three site samples exceed the background screening value of 40.64 mg/kg.

Slippage Test

K_c for zinc is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, zinc passes the Slippage test.

WRS Test

The p-level of 0.008 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, and 75th percentile are higher than the respective background values. The site interquartile range is higher than the background interquartile range. The site maximum is lower than the respective background value (Figure 1-10).

Conclusion

Because zinc in surface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

3.2 Total Soil

Twenty-three TAL metals were evaluated in the Range J total soil. Five metals (cadmium, selenium, silver, sodium and thallium) had no detectable concentrations in the total soil so no further discussion of these metals is included. Six metals (aluminum, antimony, barium, lead, manganese, and potassium) have MDCs less than their respective background screening values. Because these metals passed the Tier 1 evaluation, they will not be discussed further.

Table 2 summarizes the total soil statistical site to background comparison results. The remaining sixteen metals are carried forward for Tier 2 evaluation, and the test results are discussed below in detail. Box plots are provided in Attachment 1.

Arsenic

Tier 1 Evaluation

Nine site samples exceed the background screening value of 15.975 mg/kg.

Slippage Test

K_c for arsenic is 2, and one site sample exceeds the maximum background measurement ($K=1$). Because $K < K_c$, arsenic passes the Slippage test.

WRS Test

The p-level of < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, 75th percentile and interquartile range are much higher than that of background, and the site maximum is just slightly elevated as compared to the respective background values (Figure 1-11).

Conclusion

Because arsenic in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Beryllium

Tier 1 Evaluation

Three site samples exceed the background screening value of 0.831 mg/kg.

Slippage Test

K_c for beryllium is 2, and one site sample exceeds the maximum background measurement ($K=1$). Because $K < K_c$, beryllium passes the Slippage test.

WRS Test

The p-level of 0.011 indicates a significant difference in the site and background distributions.

Box Plot

The site minimum, maximum, and median are higher than the corresponding background values. The site interquartile range is slightly higher than the background interquartile range (Figure 1-12).

Conclusion

Because beryllium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Calcium

Tier 1 Evaluation

Two site samples exceed the background screening value of 1,204 mg/kg.

Slippage Test

K_c for calcium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, calcium passes the Slippage test.

WRS Test

The p-level of 0.7 indicates good agreement between the site and background distributions.

Box Plot

The site median is higher than the corresponding background values and the site 25th percentile, minimum and maximum are lower than the corresponding background values. (Figure 1-13).

Conclusion

Calcium in total soil is considered within the range of background.

Chromium

Tier 1 Evaluation

One site sample exceeds the background screening value of 37.6 mg/kg.

Slippage Test

K_c for chromium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, chromium passes the Slippage test.

WRS Test

The p-level of 0.008 indicates significant difference between the site and background distributions.

Box Plot

The site minimum and median are higher than the respective background values; however, the site maximum is lower than the respective background value. The site interquartile range is slightly higher than the background interquartile range (Figure 1-14).

Conclusion

Because chromium in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Cobalt

Tier 1 Evaluation

Two site samples exceed the background screening value of 16.3 mg/kg.

Slippage Test

K_c for cobalt is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, cobalt passes the Slippage test.

WRS Test

The p-level of 0.037 indicates significant difference between the site and background distributions.

Box Plot

The site minimum and median are higher than their respective background values; however, the site maximum is slightly lower than the respective background value. The site interquartile range is within the background interquartile range (Figure 1-15).

Conclusion

Because cobalt in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Copper

Tier 1 Evaluation

Ten site samples exceed the background screening value of 15.93 mg/kg.

Slippage Test

K_c for copper is 2, and one site sample exceeds the maximum background measurement ($K=1$). Because $K < K_c$, copper passes the Slippage test.

WRS Test

The p-level of < 0.001 indicates significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, and 75th percentile are higher than the respective background values; however, site maximum is similar to the respective background value. The site interquartile range is higher than background interquartile range (Figure 1-16).

Conclusion

Because copper in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Iron

Tier 1 Evaluation

Three site samples exceed the background screening value of 39,247 mg/kg.

Slippage Test

K_c for iron is 2, and one site sample exceeds the maximum background measurement ($K=1$). Because $K < K_c$, iron passes the Slippage test.

WRS Test

The p-level of 0.007 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and median are higher than the respective background values (Figure 1-17); however the site maximum is only slightly higher than the respective background value.

Conclusion

Because iron in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Magnesium

Tier 1 Evaluation

One site sample exceeds the background screening value of 905.58 mg/kg.

Slippage Test

K_c for magnesium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, magnesium passes the Slippage test.

WRS Test

The p-level of 0.267 indicates good agreement between the site and background distributions.

Box Plot

The site maximum is visibly lower with respect to background; however, the site minimum is higher than the respective background value. The site median is similar to the background median, and the site interquartile range is slightly lower than the background interquartile range (Figure 1-18).

Conclusion

Because magnesium in total soil passed statistical comparison to background, it will not be carried forward for Tier 3 geochemical evaluation.

Mercury

Tier 1 Evaluation

Four site samples exceed the background screening value of 0.0704 mg/kg.

Slippage Test

K_c is 2 for mercury, and no site samples exceed the maximum background measurement ($K=0$). Since $K < K_c$, mercury passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

Box Plot

The site minimum, median, 25th percentile, and 75th percentile are elevated relative to the corresponding background values (Figure 1-19). The shape and location of the background box plot is influenced by the percentage of nondetects (60 percent), and the replacement values of one-half the reporting limit rather than detected concentrations. The site maximum is significantly lower than the respective background value.

Hot Measurement Test

The site MDC of mercury exceeds the background 95th percentile of 0.094 mg/kg.

Conclusion

Because mercury in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Nickel

Tier 1 Evaluation

Seven samples exceed the background screening value of 11.56 mg/kg.

Slippage Test

K_c for nickel is 2 and one site samples exceed the maximum background measurement ($K=1$). Since $K < K_c$, nickel passes the Slippage test.

WRS Test

The p-level of < 0.001 indicates a difference between the site and background distributions.

Box Plot

The site minimum, maximum, 25th percentile, 75th percentile, and median are higher than the respective background values (Figure 1-20).

Conclusion

Because nickel in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Vanadium

Tier 1 Evaluation

Four site samples exceed the background screening value of 61.734 mg/kg.

Slippage Test

K_c for vanadium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, vanadium passes the Slippage test.

WRS Test

The p-level of < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, 25th percentile, 75th percentile, and median are visibly higher than the respective background values (Figure 1-21); however, the site maximum is lower than the respective background value.

Conclusion

Because vanadium failed in total soil statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Zinc

Tier 1 Evaluation

Eleven site samples exceed the background screening value of 37.88 mg/kg.

Slippage Test

K_c for zinc is 2, and two site samples exceed the maximum background measurement ($K=2$). Because $K \leq K_c$, zinc passes the Slippage test.

WRS Test

The p-level of < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, 75th percentile, and maximum values are visibly higher than the respective background values. The site interquartile range is higher than background interquartile range (Figure 1-22).

Conclusion

Because zinc in total soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

3.3 Groundwater

This section presents the results of the site-to-background comparisons for 23 metals in unfiltered groundwater samples. Eight metals (antimony, beryllium, cadmium, cobalt, copper, mercury, silver, and thallium) had no detects in the groundwater site samples and are not

considered any further. Ten metals (arsenic, barium, chromium, iron, lead, manganese, nickel, selenium, vanadium and zinc) had no detected concentrations that exceeded their respective background screening values. These metals are considered within the background range based on the Tier 1 evaluation, and will not be tested or discussed further. Table 3 summarizes these results.

The remaining metals (aluminum, calcium, magnesium, potassium, and sodium) are carried forward for Tier 2 evaluation. The results of this evaluation are summarized in Table 3 and discussed in detail below. Box plots are provided in Attachment 1.

Aluminum

Tier 1 Evaluation

One sample exceeds the background screening value of 2.335 mg/L.

Slippage Test

K_c for aluminum is 3, and no site sample exceeds the maximum background measurement ($K=0$). Because $K < K_c$, aluminum passes the Slippage test.

WRS Test

The p-level of 0.455 indicates good agreement between the site and background distributions.

Box Plot

The site minimum is elevated as compared to the corresponding background values. The site maximum and median are lower than the corresponding background values. The site interquartile range is within the background interquartile range (Figure 1-23).

Conclusion

Aluminum in groundwater is considered within the range of background.

Calcium

Tier 1 Evaluation

One sample exceeds the background screening value of 56.493 mg/L.

Slippage Test

K_c for calcium is 3, and no site sample exceeds the maximum background measurement. Because $K < K_c$, calcium passes the Slippage test.

WRS Test

The p-level of 0.55 indicates good agreement between the site and background distributions.

Box Plot

The site minimum is elevated as compared to the corresponding background value. The site maximum is lower than the corresponding background value. The site interquartile range is within the background interquartile range, and the site median is slightly higher than the corresponding background value (Figure 1-24).

Conclusion

Calcium in groundwater is considered within the range of background.

Magnesium

Tier 1 Evaluation

One sample exceeds the background screening value of 21.282 mg/L.

Slippage Test

K_c for magnesium is 3, and no site sample exceeds the maximum background measurement. Because $K < K_c$, magnesium passes the Slippage test.

WRS Test

The p-level of <0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, median, 25th percentile, and 75th percentile are elevated as compared to the corresponding background values. The site maximum is lower than the corresponding background values. (Figure 1-25).

Conclusion

Because magnesium failed in groundwater statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Potassium

Tier 1 Evaluation

Nine samples exceed the background screening value of 7.195 mg/L.

Slippage Test

K_c for potassium is 3, and two site samples exceed the maximum background measurement. Because $K < K_c$, potassium passes the Slippage test.

WRS Test

The WRS test was not performed because the site data set contains more than 50 percent nondetects.

Box Plot

The site minimum, maximum, median, 25th percentile, and 75th percentile are elevated as compared to the corresponding background values. The site interquartile range is higher than the background interquartile range (Figure 1-26).

Hot Measurement Test

The site MDC of potassium exceeds the background 95th percentile of 16 mg/L.

Conclusion

Because potassium failed in groundwater statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Sodium

Tier 1 Evaluation

Three samples exceed the background screening value of 14.846 mg/L.

Slippage Test

K_c for sodium is 3, and no site sample exceeds the maximum background measurement.

Because $K < K_c$, sodium passes the Slippage test.

WRS Test

The p-level of 0.848 indicates good agreement between the site and background distributions.

Box Plot

The site minimum is elevated as compared to the corresponding background value. The site maximum is slightly lower than the corresponding background value. The site interquartile range is slightly lower than the background interquartile range (Figure 1-27).

Conclusion

Sodium in groundwater is considered within the range of background.

4.0 Summary and Conclusions

The statistical methodology used to compare the Range J, Parcel 202(7) and background data sets for 23 elements in surface soil, total soil, and groundwater includes a comparison of the site MDC to the background screening value (i.e., Tier 1 evaluation). Analytes that failed this comparison were subjected to the Slippage test and WRS test. Box-and-whisker plots were prepared to visually compare the two data sets and properly interpret the WRS test results. For elements with data sets that did not allow for either the Slippage test or WRS test to be performed, the Hot Measurement test was used. Analytes that failed these statistical tests, Tier 2 evaluation, are carried forward for Tier 3 geochemical evaluation to determine if natural processes can explain the elevated concentrations.

Tables 1 through 3 summarize the comparison test results and show the metals carried forward for geochemical evaluation.

5.0 References

Rosenbaum, S., 1954, "Tables for a Nonparametric Test of Location," *Annals of Mathematical Statistics*, Vol. 24, pp. 146-150.

Science Application International Corporation (SAIC), 1998, *Final Background Metals Survey Report, Fort McClellan, Anniston, Alabama*, prepared for U.S. Army Corps of Engineers, Mobile, Alabama, July.

Shaw Environmental and Infrastructure (Shaw E&I), 2003, *Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2*, Technical Memorandum, 24 June 2003 by Paul Goetchius.

U.S. Environmental Protection Agency (EPA), 1989, *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Interim Final Guidance*, Office of Solid Waste, Waste Management Division, EPA/530/SW-89/026, July.

U.S. Environmental Protection Agency (EPA), 1992, *Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance*, Environmental Statistics and Information Division, Office of Policy, Planning, and Evaluation, EPA/530/R-93/003, July.

U.S. Environmental Protection Agency (EPA), 1994, *Statistical Methods For Evaluating The Attainment Of Cleanup Standards*, Environmental Statistics and Information Division, Office of Policy, Planning, and Evaluation, EPA/230/R-94/004, June.

U.S. Environmental Protection Agency (EPA), 2000, *Guidance for Data Quality Assessment: Practical Methods for Data Analysis, EPA QA/G-9, QA00 Update*, Office of Environmental Information, EPA/600/R-96/084, July.

U.S. Navy, 2002, *Guidance for Environmental Background Analysis, Volume 1: Soil*, NFESC User's Guide UG-2049-ENV, Naval Facilities Engineering Command, Washington, D.C., April.

ATTACHMENT 1

Figure 1-1. Box Plot Comparison for Arsenic in Surface Soil
Fort McClellan, Range J
(WRS Test p-level = 0.002)

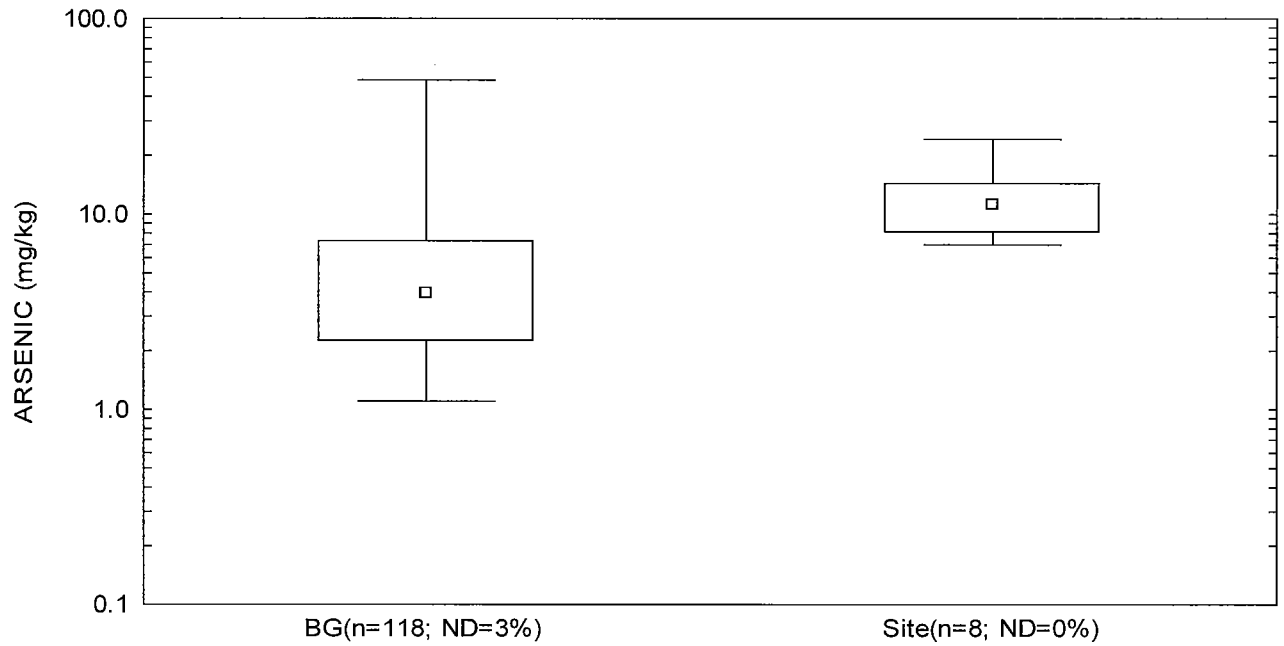


Figure 1-2. Box Plot Comparison for Calcium in Surface Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.059)

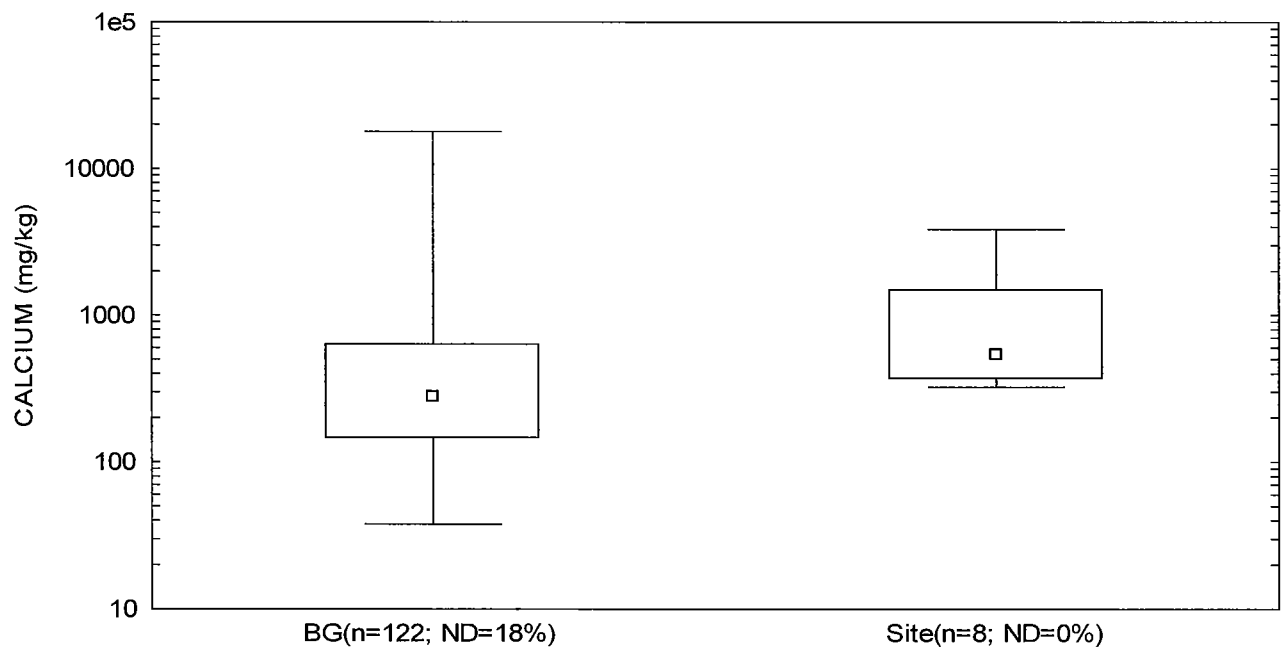


Figure 1-3. Box Plot Comparison for Chromium in Surface Soil

Ft. McClellan, Range J

(WRS Test p-level = 0.008)

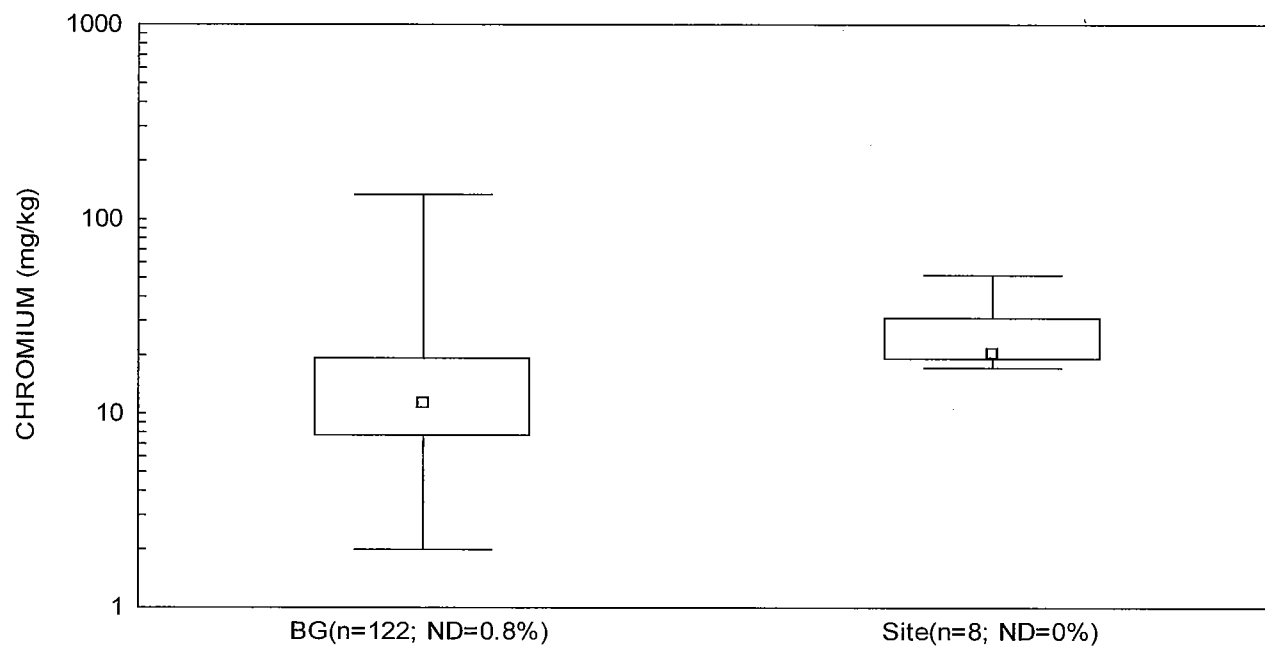


Figure 1-4. Box Plot Comparison for Copper in Surface Soil

Ft. McClellan, Range J

(WRS Test p-level = 0.018)

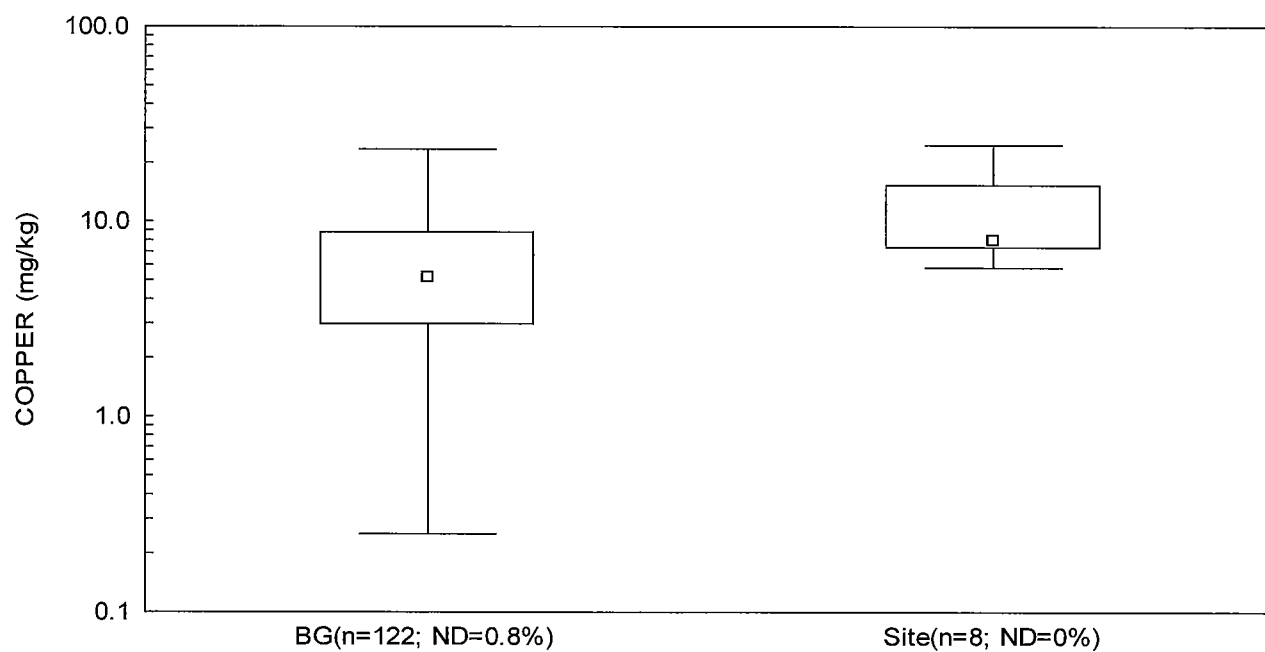


Figure 1-5. Box Plot Comparison for Iron in Surface Soil

Ft. McClellan, Range J

(WRS Test p-level = 0.103)

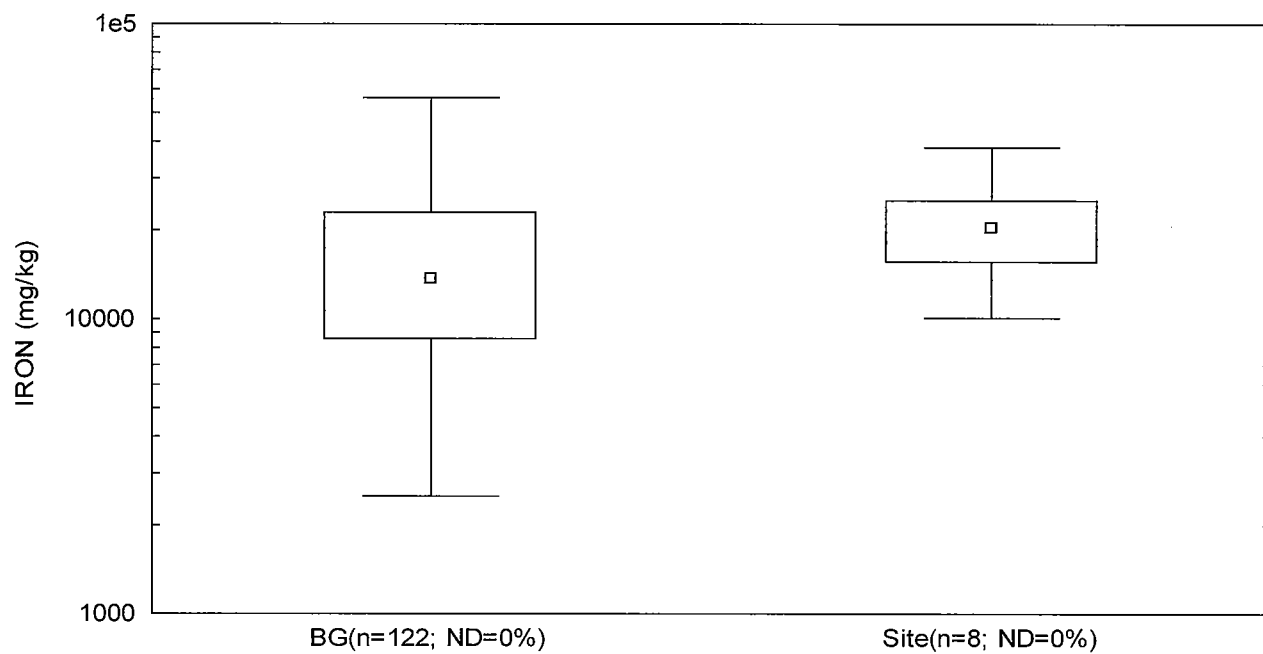


Figure 1-6. Box Plot Comparison for Magnesium in Surface Soil

Ft. McClellan, Range J

(WRS Test p-level = 1)

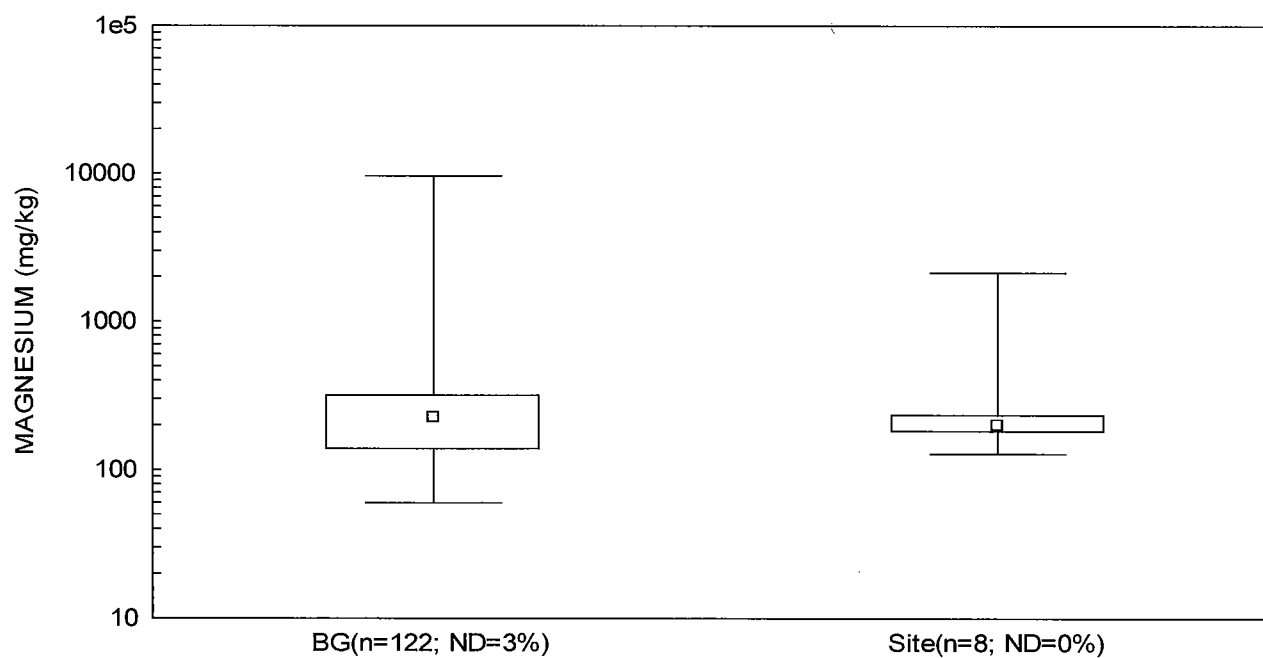


Figure 1-7. Box Plot Comparison for Mercury in Surface Soil
Ft. McClellan, Range J

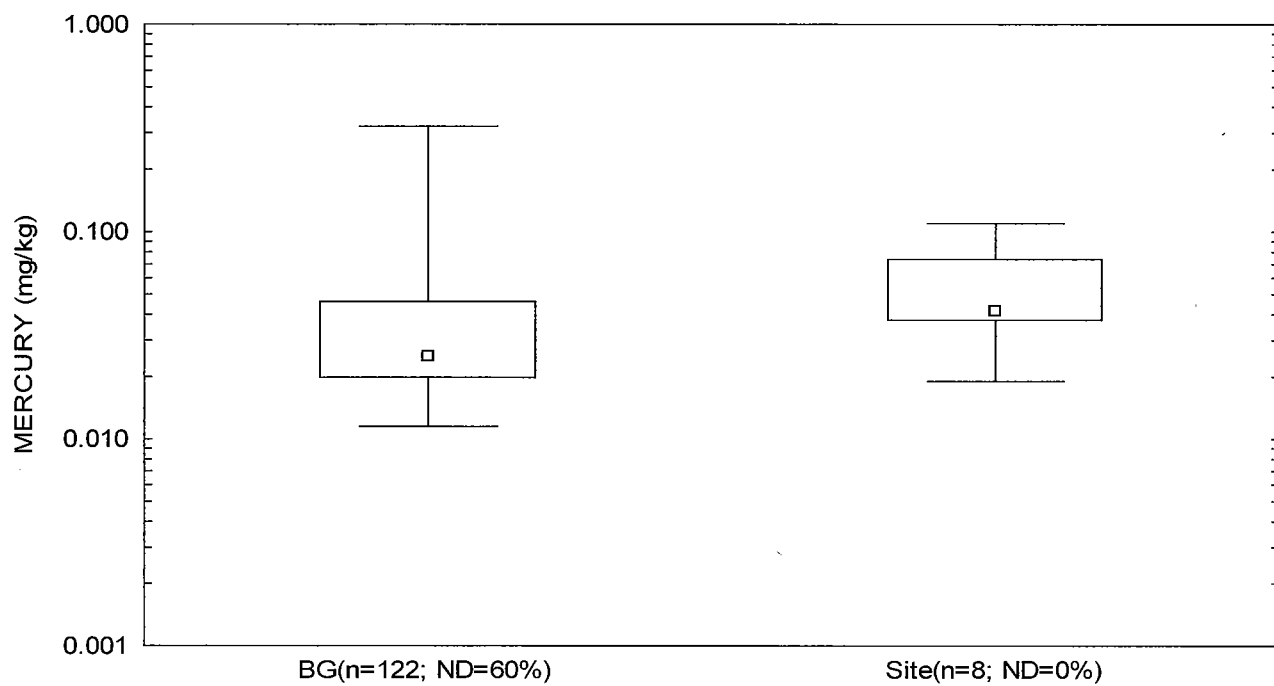


Figure 1-8. Box Plot Comparison for Nickel in Surface Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.192)

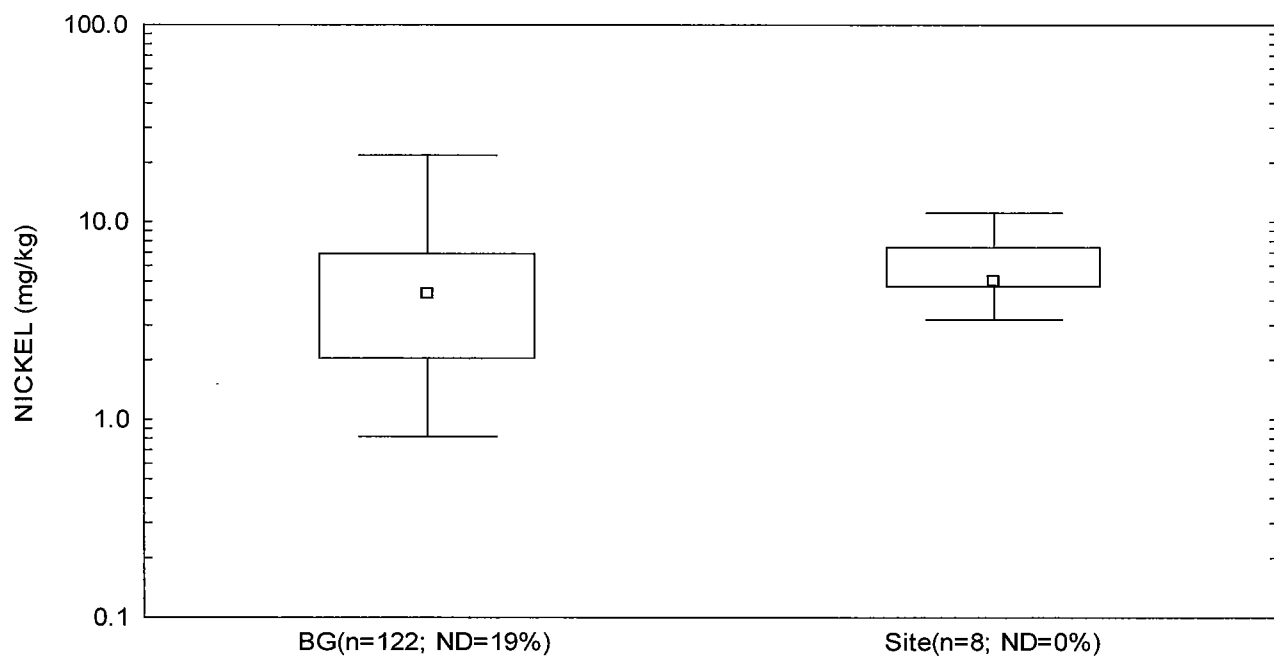


Figure 1-9. Box Plot Comparison for Vanadium in Surface Soil

Ft. McClellan, Range J

(WRS Test p-level = 0.018)

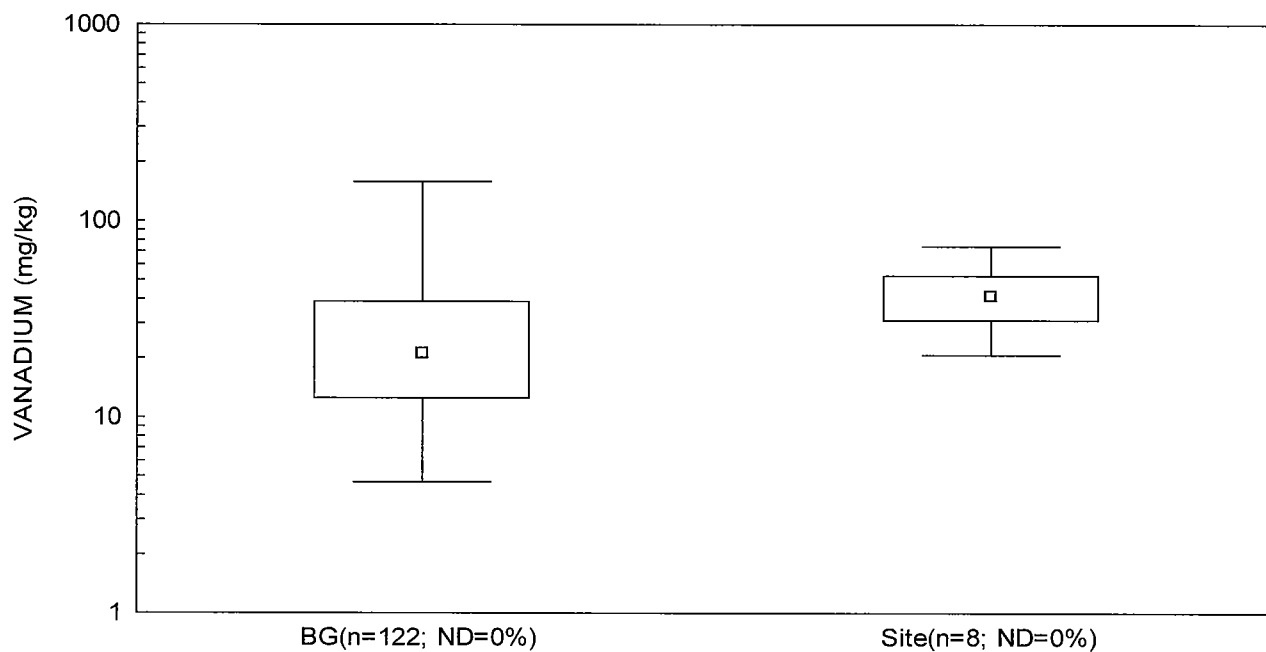


Figure 1-10. Box Plot Comparison for Zinc in Surface Soil

Ft. McClellan, Range J

(WRS Test p-level = 0.008)

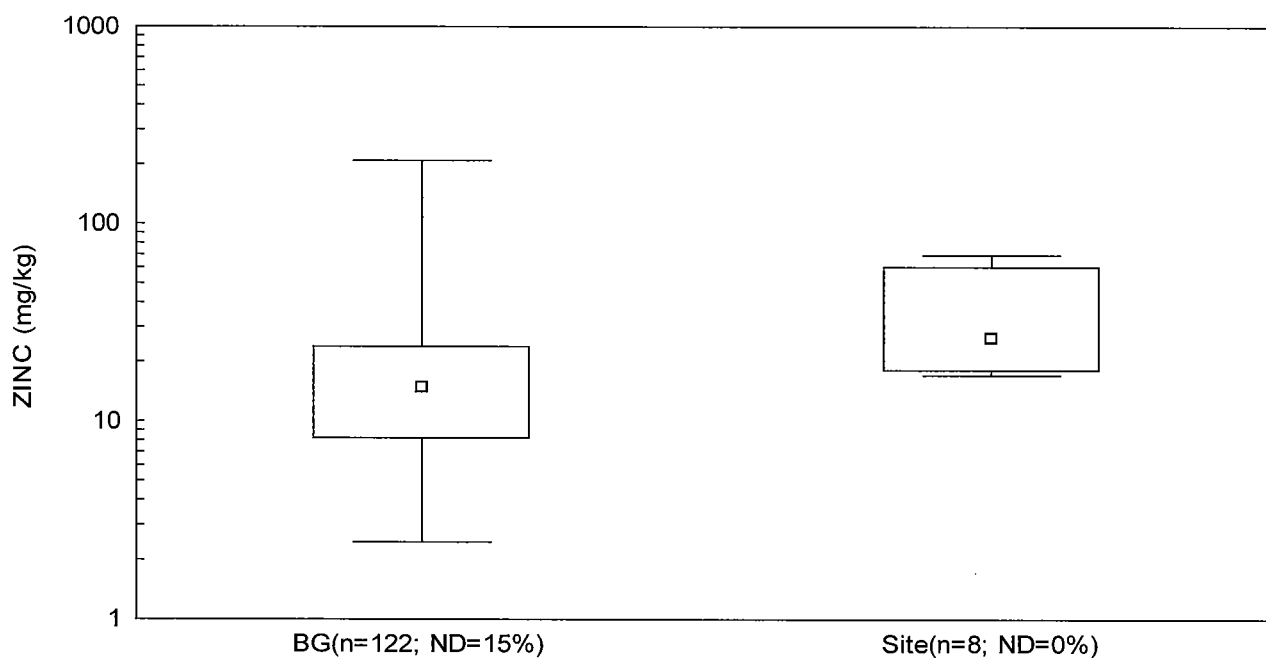


Figure 1-11. Box Plot Comparison for Arsenic in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level < 0.001)

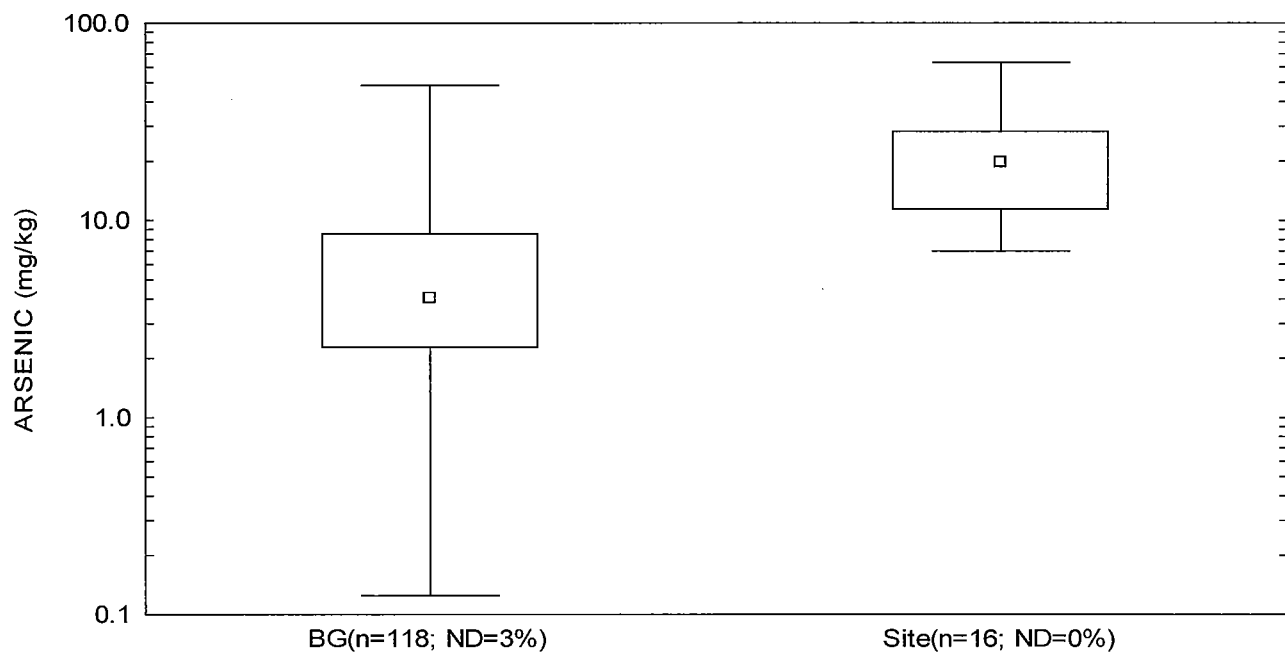


Figure 1-12. Box Plot Comparison for Beryllium in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.011)

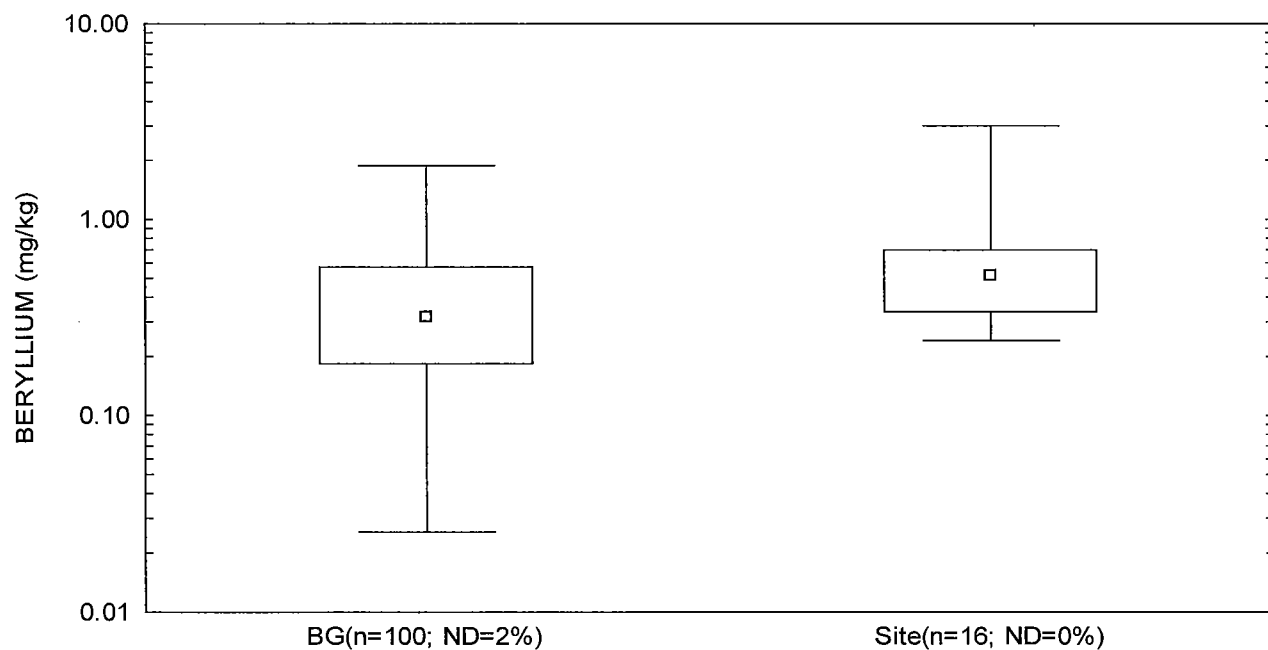


Figure 1-13. Box Plot Comparison for Calcium in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.699)

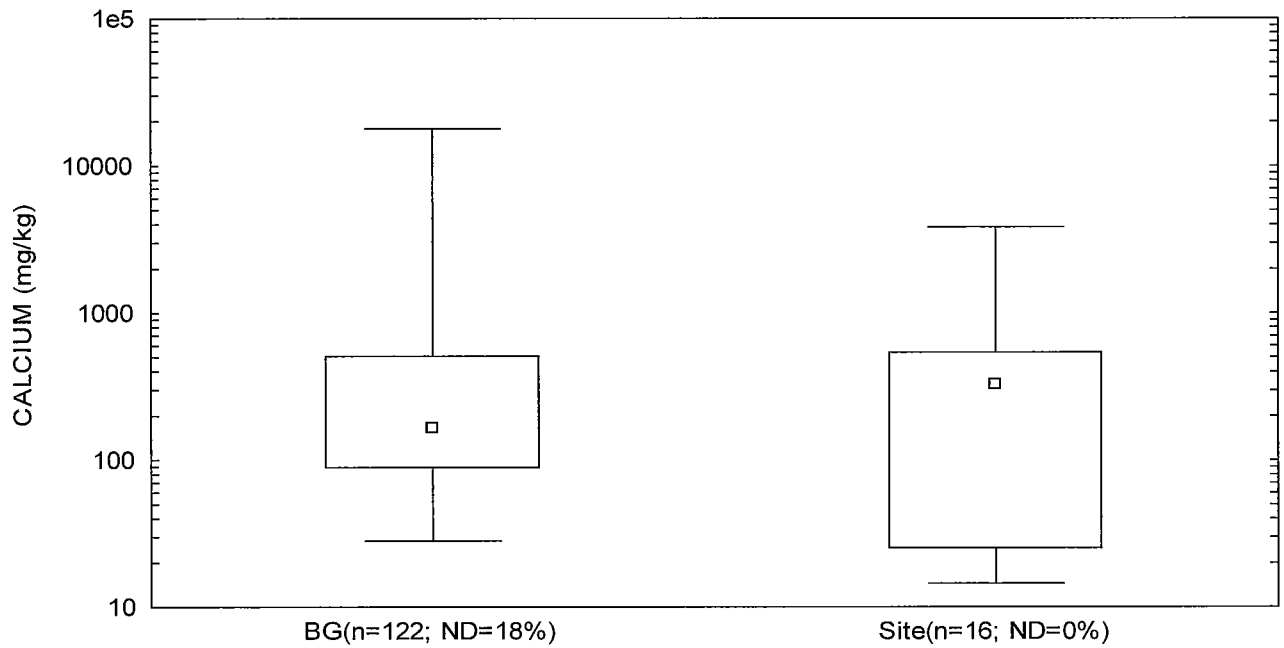


Figure 1-14. Box Plot Comparison for Chromium in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.008)

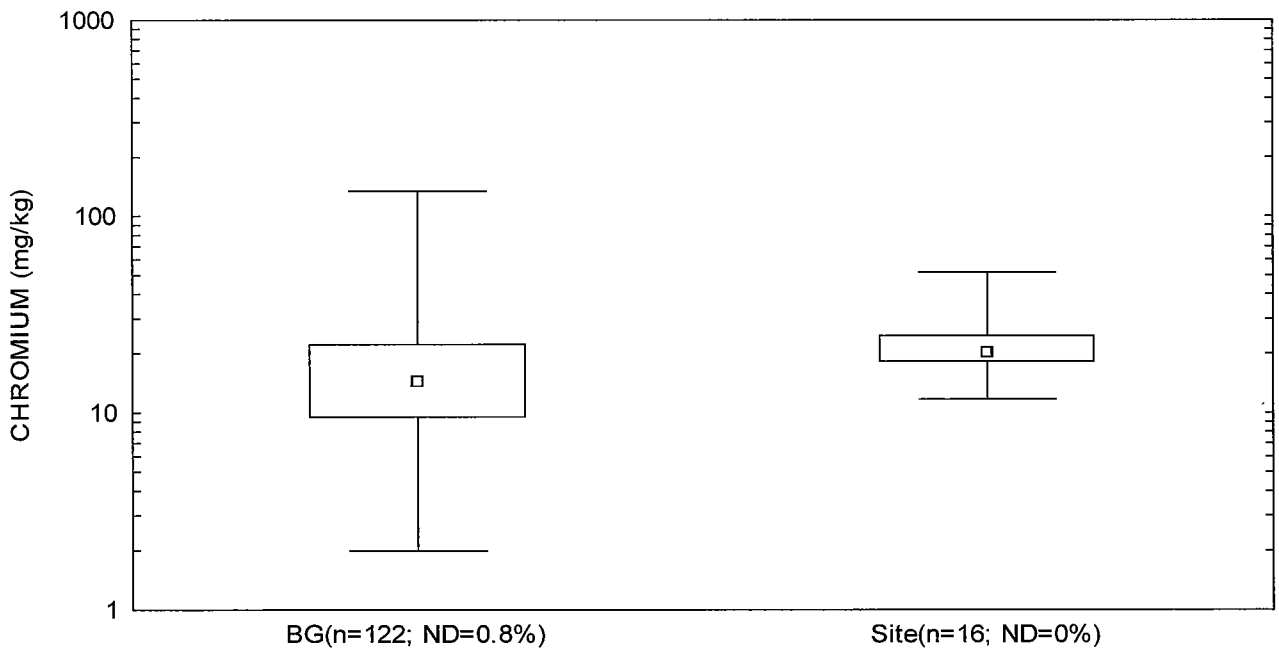


Figure 1-15. Box Plot Comparison for Cobalt in Combined Soil

Ft. McClellan, Range J

(WRS Test p-level = 0.037)

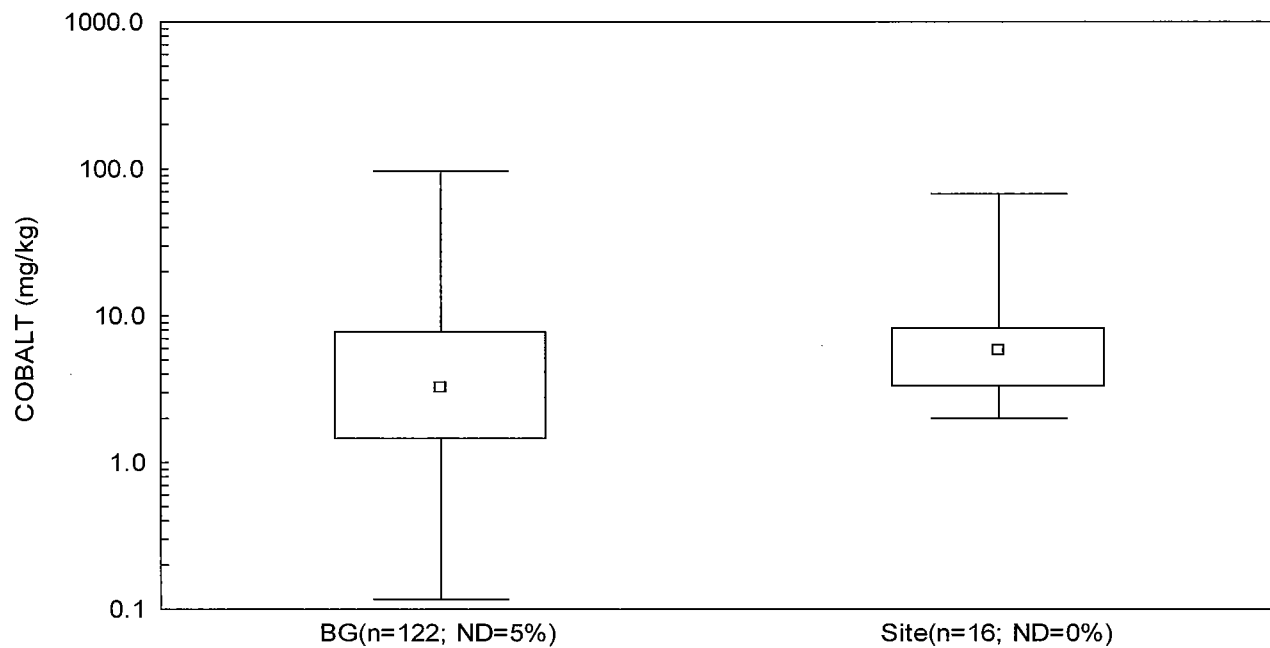


Figure 1-16. Box Plot Comparison for Copper in Combined Soil

Ft. McClellan, Range J

(WRS Test p-level < 0.001)

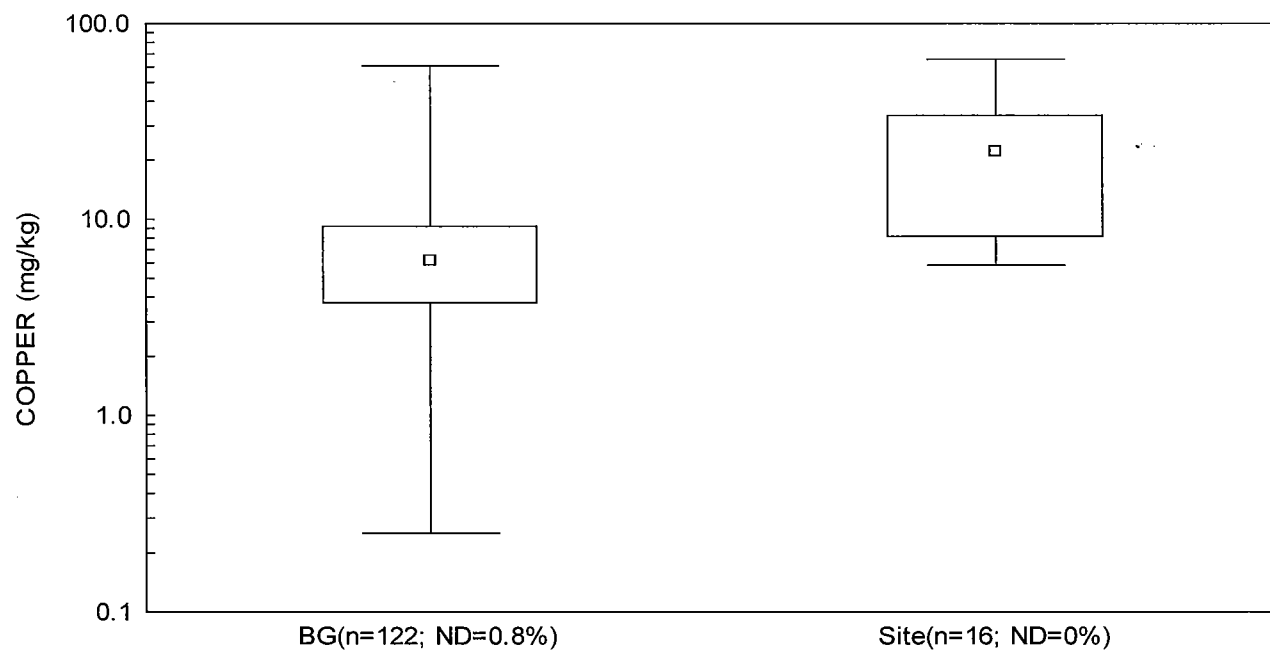


Figure 1-17. Box Plot Comparison for Iron in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.007)

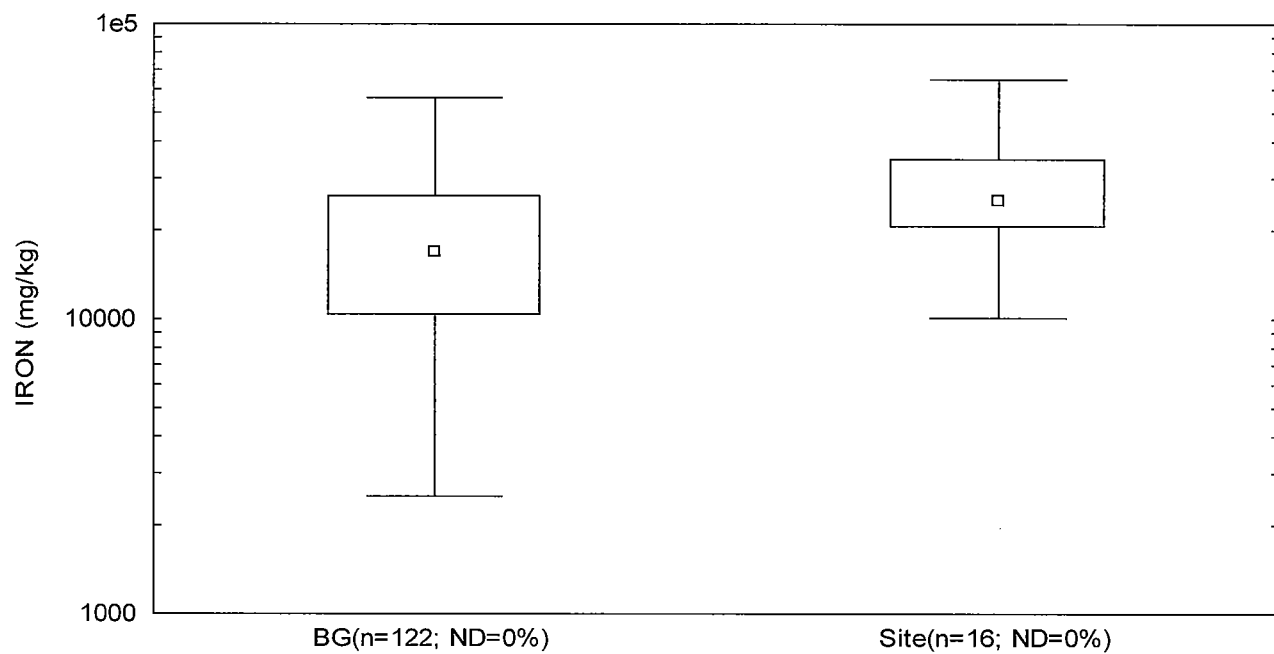


Figure 1-18. Box Plot Comparison for Magnesium in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level = 0.267)

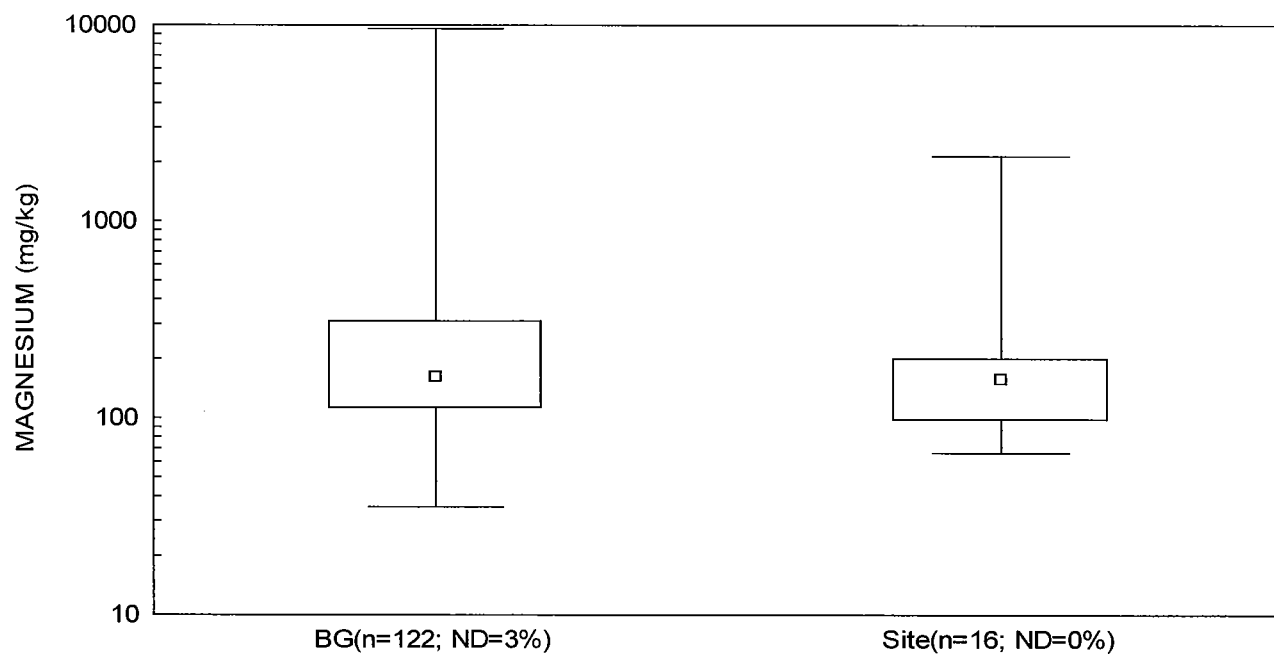


Figure 1-19. Box Plot Comparison for Mercury in Combined Soil
Ft. McClellan, Range J

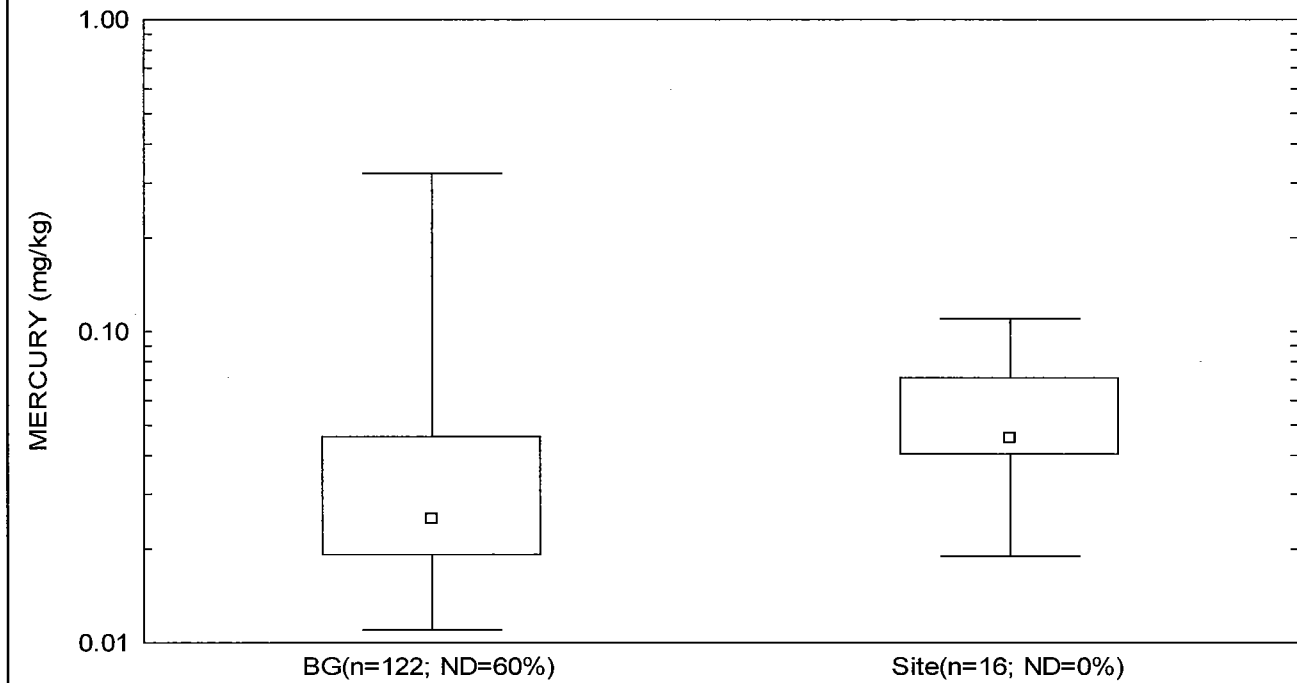


Figure 1-20. Box Plot Comparison for Nickel in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level < 0.001)

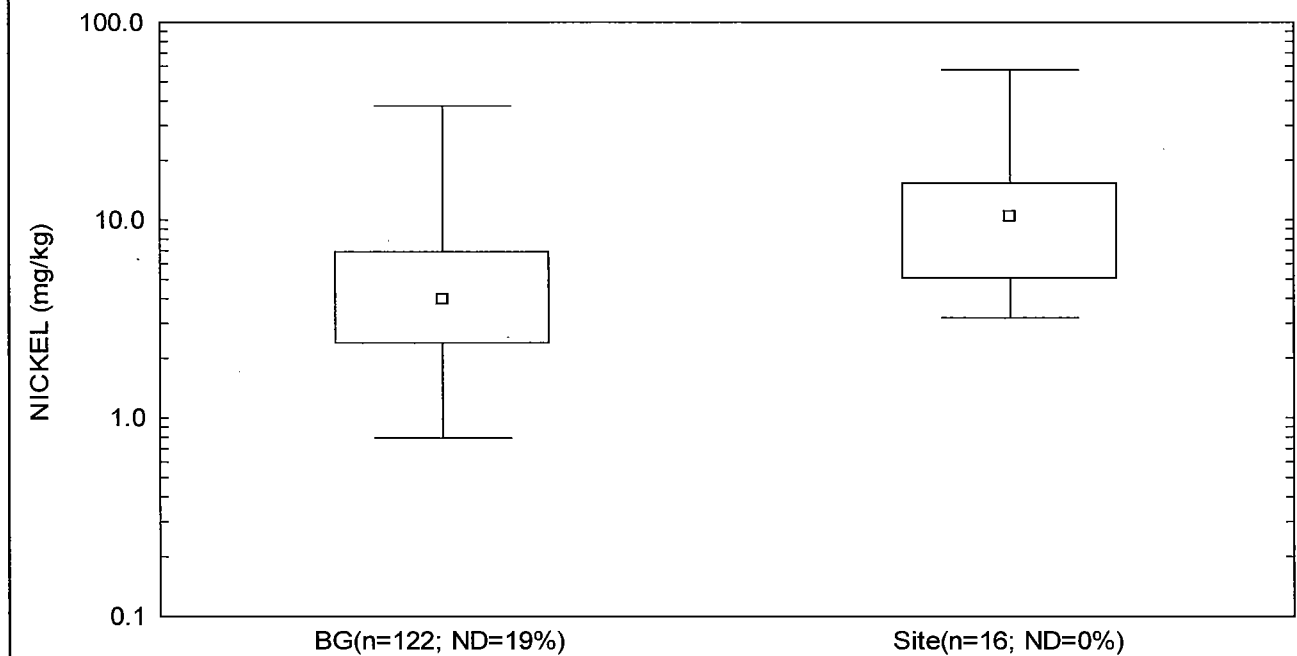


Figure 1-21. Box Plot Comparison for Vanadium in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level < 0.001)

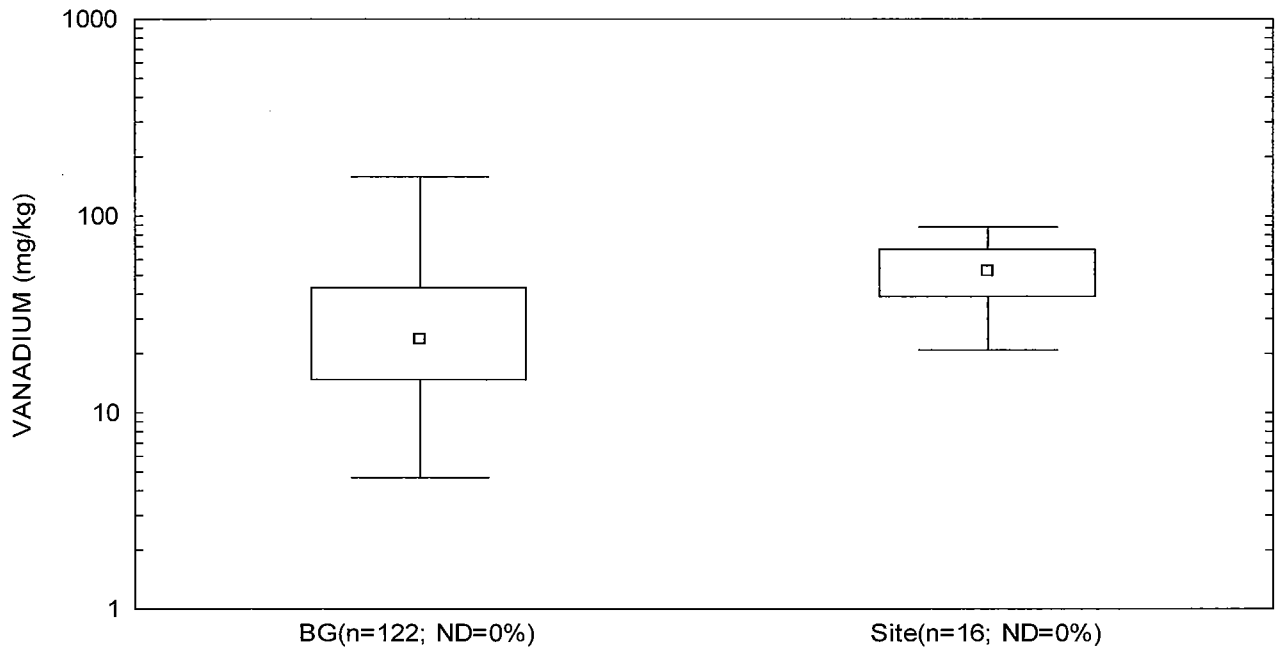


Figure 1-22. Box Plot Comparison for Zinc in Combined Soil
Ft. McClellan, Range J
(WRS Test p-level < 0.001)

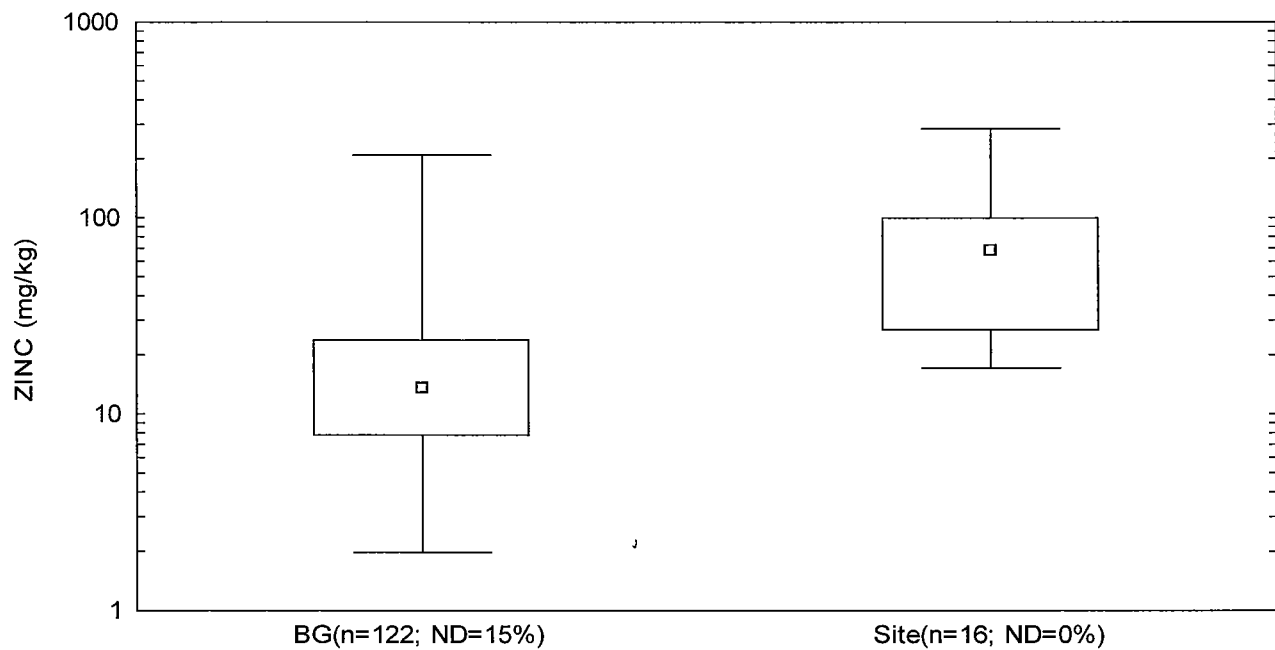


Figure 1-23. Box Plot comparison for Aluminum in Groundwater

Ft. McClellan, Range J

(WRS Test p-level = 0.455)

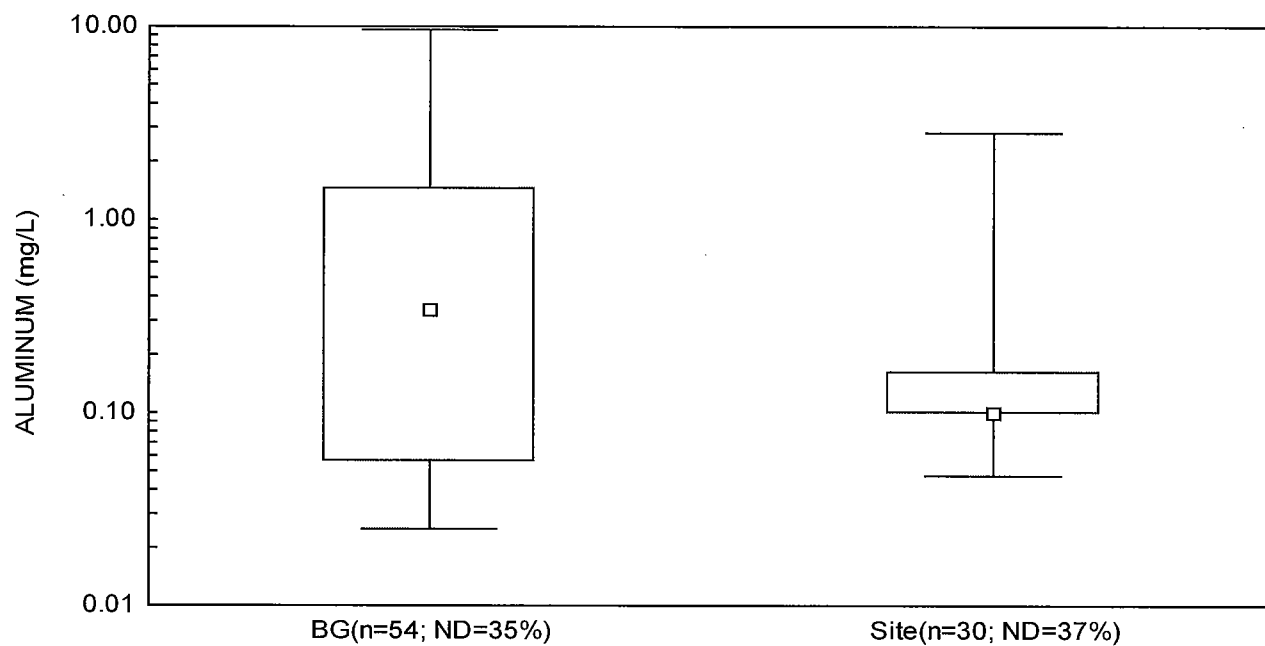


Figure 1-24. Box Plot Comparison for Calcium in Groundwater

Ft. McClellan, Range J

(WRS Test p-level = 0.55)

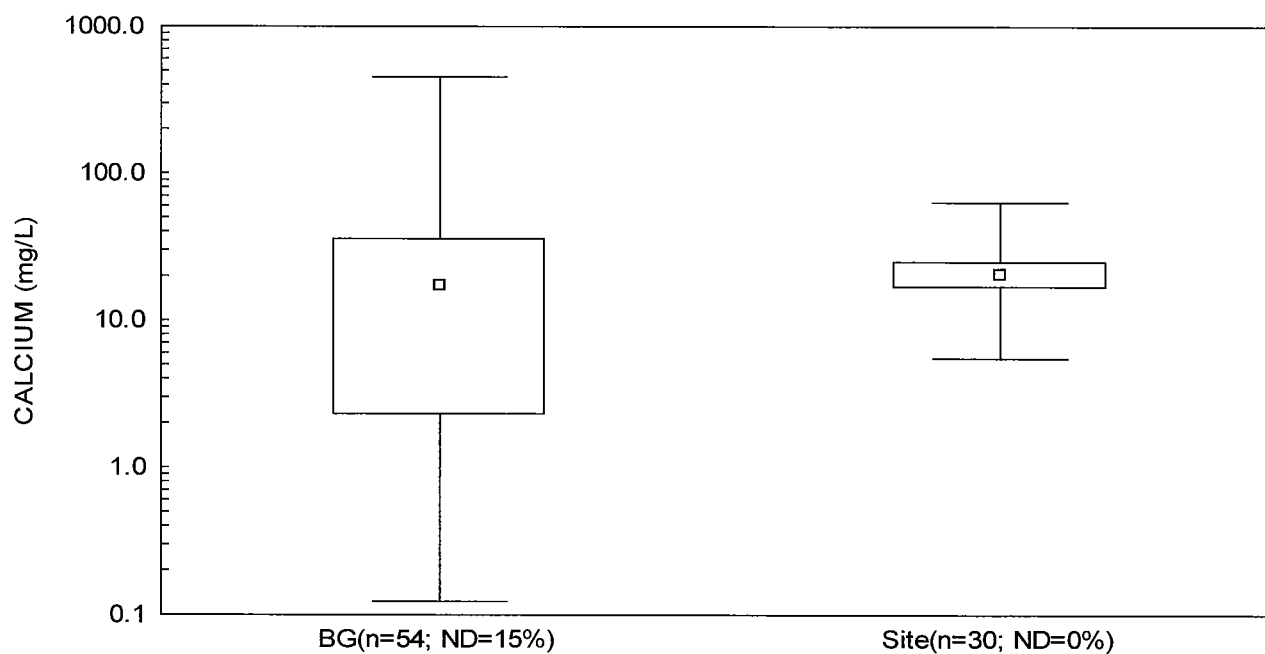


Figure 1-25.Box Plot Comparison for Magnesium in Groundwater
Ft. McClellan, Range J
(WRS Test p-level < 0.001)

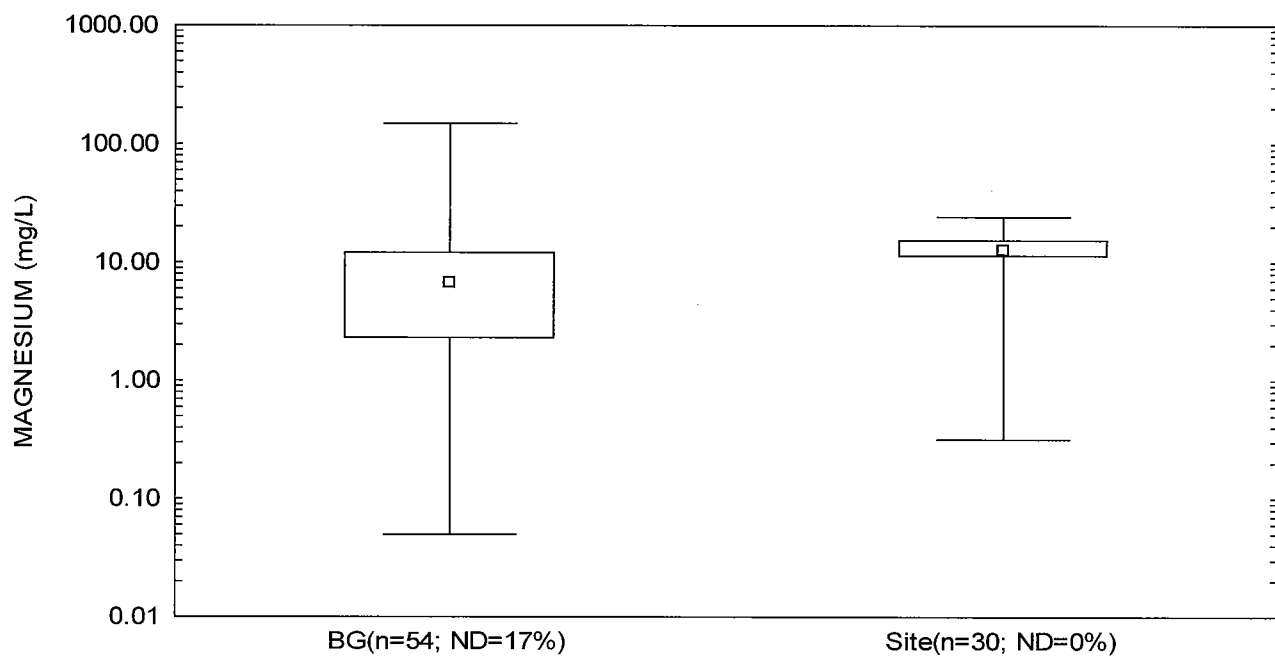


Figure 1-26. Box Plot Comparison for Potassium in Groundwater
Ft. McClellan, Range J

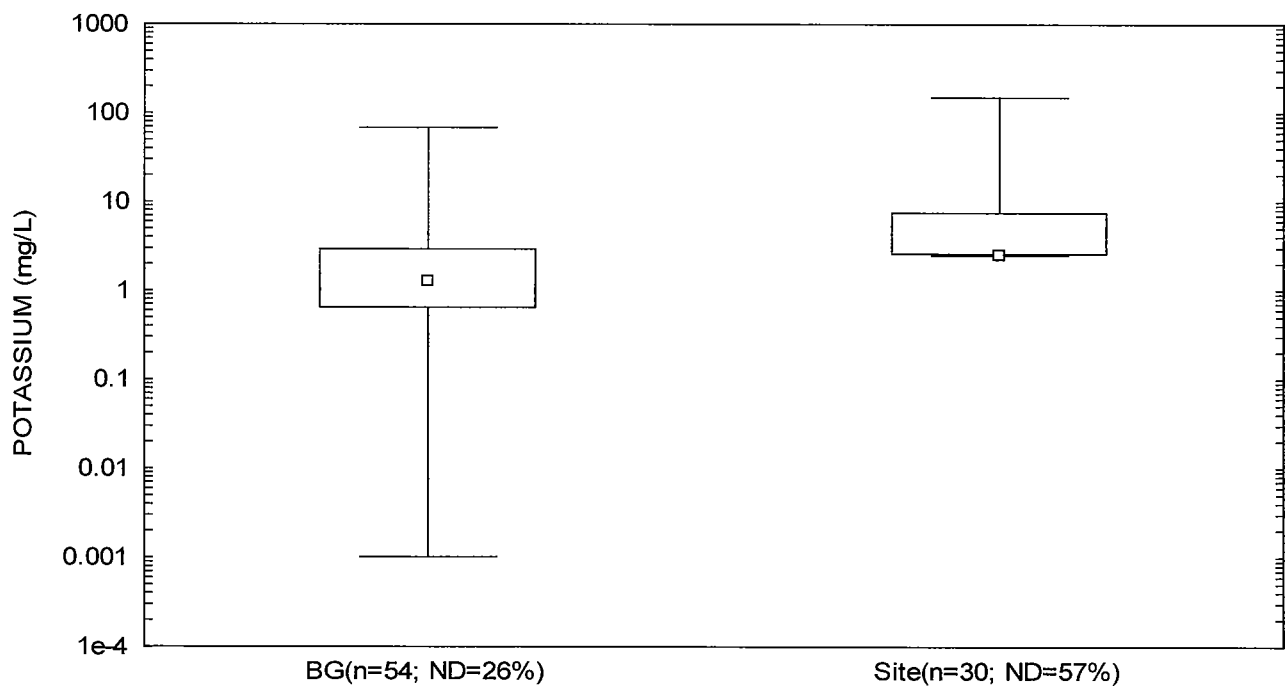
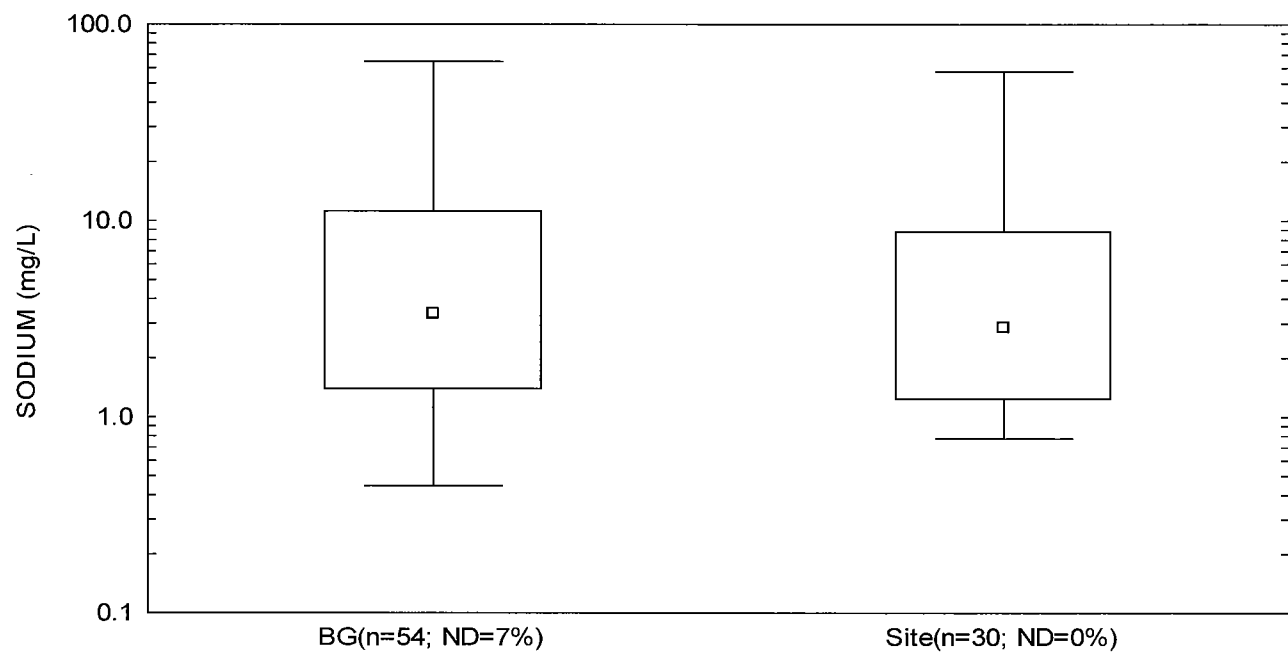


Figure 1-27. Box Plot Comparison for Sodium in Groundwater

Ft. McClellan, Range J

(WRS Test p-level = 0.848)



GEOCHEMICAL

Final

Remedial Investigation Report
Range J – Pelham Range, Parcel 202(7)

Volume II of II
Appendices D through L

Fort McClellan
Calhoun County, Alabama

Prepared for:

U.S. Army Corps of Engineers, Mobile District
109 St. Joseph Street
Mobile, Alabama 36602

Prepared by:

Shaw Environmental, Inc.
312 Directors Drive
Knoxville, Tennessee 37923

Task Order CK05
Contract No. DACA21-96-D-0018
Shaw Project No. 774645

October 2003

Revision 0

Geochemical Evaluation of Metals in Soil and Groundwater at Range J, Parcel 202(7) Fort McClellan, Alabama

1.0 Introduction

This report provides the results of a geochemical evaluation of inorganic constituents in soil and groundwater samples from Range J, Parcel 202(7), Fort McClellan, Calhoun County, Alabama. Eleven elements in soil and two elements in groundwater failed statistical comparison to background. A geochemical evaluation was performed to determine if the elevated concentrations are naturally occurring or if they contain a component of contamination.

Site samples included in the evaluations consist of eight surface soil samples (0 to 1 foot below ground surface [bgs]) collected in June 2001, eight subsurface soil samples (11 to 12 feet bgs) collected in June 2001, and thirty unfiltered groundwater samples collected in May 2001. All of the site samples were analyzed for the full list of 23 target analyte list (TAL) metals.

Installation-wide background data for TAL metals in soil, sediment, groundwater, and surface water are provided in the background study report (Science Applications International Corporation, 1998) and are used in the following evaluations.

2.0 Geochemical Evaluation Methodology

Naturally occurring trace element concentrations in environmental media commonly exceed regulatory screening criteria. For example, trace element distributions in uncontaminated soil tend to have very large ranges (two to three orders of magnitude are not uncommon), and are highly right-skewed, resembling lognormal distributions. These trace elements are naturally associated with specific soil-forming minerals, and the preferential enrichment of a sample with these minerals will result in elevated trace element concentrations. It is thus important to be able to identify these naturally high concentrations and distinguish them from potential contamination.

If an analyte fails statistical comparison to background as described in the “Statistical Comparison of Site and Background Data for Range J, Parcel 202(7),” then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (U.S. Environmental Protection

Agency, 1995; Barclift, *et al.*, 2000; U.S. Navy, 2002; Myers and Thorbjornsen, 2004). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent contamination can also be readily distinguished from uncontaminated samples. This section describes the geochemical evaluation techniques that were employed in the Range J site-to-background comparisons.

It should be noted that the geochemical evaluations rely in part on professional judgment and qualitative assessment is a necessary part of the process. Samples that plot off the linear trend on a correlation plot are certainly suspect, but because all uncertainty cannot be eliminated from the evaluation, such plots cannot be construed as definitive proof of contamination. However, anomalous samples should be flagged as suspect and their results used as a basis for further investigation, risk assessment, or remediation, as appropriate. The combination of statistical evaluations (Tiers 1 and 2) and geochemical evaluation (Tier 3) as presented in this appendix is effective in reducing the occurrences of decision errors relative to consideration of statistics or geochemistry alone.

2.1 Soil

The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil matrix. As an example, arsenic in most uncontaminated oxic soils is almost exclusively associated with iron oxide minerals (Bowell, 1994; Schiff and Weisberg, 1997). (The term “iron oxide” is used here to include oxides, hydroxides, oxyhydroxides, and hydrous oxides of iron.) This association of arsenic with iron oxides is a result of the adsorptive behavior of this particular trace metal in an oxic soil environment. Arsenic is present in oxic soil pore fluid as negatively charged oxyanions (HAsO_4^{-2} , H_2AsO_4^-) (Brookins, 1988). These anions have strong affinities to adsorb on the surfaces of iron oxides, which maintain a strong positive surface charge (Electric Power Research Institute, 1986). If a soil sample has a high percentage of iron oxides, then it is expected to have a proportionally higher concentration of arsenic.

The absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in the samples are usually quite constant as long as no contamination is present (Daskalakis and O'Connor, 1995). If a sample has some naturally occurring arsenic plus additional arsenic from an herbicide or some other source, then it will have an anomalously high ratio relative to the other uncontaminated samples. These ratios thus serve as a powerful technique for identifying contaminated samples.

The evaluation includes the generation of plots in which detected arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding detected iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average arsenic/iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by the preferential enrichment of iron oxides in those samples. If the site samples with elevated arsenic concentrations plot above the trend displayed by the uncontaminated samples, then there is evidence that those samples have an excess contribution of arsenic, and contamination may be indicated.

Each trace element is associated with one or more minerals in the soil matrix. Vanadium and selenium, along with arsenic, form anionic species in solution and are associated with iron oxides, which maintain a positive surface charge. Divalent metals such as barium, cadmium, lead, and zinc tend to form cationic species in solution and are attracted to clay mineral surfaces, which maintain a negative surface charge. These trace elements would be evaluated against aluminum, which is a major component of clay minerals. Manganese oxides also have an affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). These trace elements would be evaluated against manganese.

2.2 Groundwater

Elevated concentrations of inorganic constituents in groundwater samples may be due to naturally high dissolved concentrations, the presence of suspended particulates in the samples, reductive dissolution, or contamination resulting from site activities. One primary mechanism that is examined in the Ft. McClellan groundwater site-to-background comparisons is the presence of suspended particulates, as discussed below.

Effects of Suspended Particulates. The presence of trace elements adsorbed on suspended particulates can greatly increase trace element concentrations as reported by an analytical laboratory. These adsorbed trace elements are not in true solution, and can be removed by settling or filtration. The same concepts involved in the evaluation of soil data also apply to groundwater data: samples containing trace elements adsorbed on suspended clay particulates should show a positive correlation with aluminum concentrations, and samples containing trace elements adsorbed on suspended iron oxides should show a positive correlation with iron concentrations. These correlations are evaluated by generating x-y plots of the concentrations of an elevated trace metal versus aluminum or iron (depending on the trace element).

The most common suspended particulates in groundwater samples are clay minerals; hydrous aluminum oxides ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) and hydroxides [$\text{Al}(\text{OH})_3$]; and iron oxide (Fe_2O_3), iron hydroxide [$\text{Fe}(\text{OH})_3$], and iron oxyhydroxide ($\text{FeO} \cdot \text{OH}$) minerals, collectively referred to as “iron oxides.” All clay minerals contain aluminum and have low solubilities over a neutral pH range of 6 to 8. Measured concentrations of aluminum in excess of ~1 milligram per liter (mg/L) indicate the presence of suspended clay minerals (Hem, 1985; Stumm and Morgan, 1996), with higher aluminum concentrations being a qualitative indicator of the mass of suspended clay minerals. Iron also has a very low solubility under neutral pH and moderate to oxidizing redox conditions, so that measured iron concentrations in excess of ~1 mg/L under these conditions indicate the presence of suspended iron oxides (Hem, 1985).

The presence of suspended clay or iron oxides in groundwater samples has particular importance in the interpretation of trace element concentrations. Most clay particles maintain a negative surface charge under neutral pH conditions, and have a strong tendency to adsorb positively charged (cationic) aqueous species. Iron oxides display the opposite behavior, maintaining a positive surface charge under neutral pH conditions, and have a strong tendency to adsorb negatively charged (anionic) aqueous species.

Barium, lead, and zinc are usually present in groundwater as divalent cations and thus tend to concentrate on clay surfaces (EPRI, 1984; Brookins, 1988). Arsenic, selenium, and vanadium are usually present under oxidizing conditions as oxyanions, and thus tend to concentrate on iron oxide surfaces (Bowell, 1994; Hem, 1985; Pourbaix, 1974; Brookins, 1988).

Chromium can be present in groundwater as a mixture of aqueous species with different charges, depending on pH (EPRI, 1984). The positive, neutral, and negative charges on these species result in the distribution of chromium on several different types of sorptive surfaces, including clay and iron oxide minerals.

As an example, the concentrations of zinc (y-axis) would be plotted against aluminum (x-axis). If all of the samples display a common linear trend, then it is most likely that the zinc concentrations are due to the presence of suspended clay minerals in the samples. The slope of a best-fit line through the points is equal to the average zinc/aluminum ratio. If some samples plot above the linear trend established by the other samples, then those samples have an anomalously high zinc/aluminum ratio, and most likely contain excess zinc that cannot be explained by these natural processes.

Alternative techniques for assessing the effects of suspended particulates on trace element concentrations are the evaluation of correlations of trace element concentrations versus turbidity, and comparison of analyses of filtered versus unfiltered splits of samples. Turbidity measurements are qualitative; do not distinguish between suspended clay minerals, iron oxides, and natural organic material; and are affected by the size and shape of suspended particulates, so this approach lacks the resolution provided by trace element versus aluminum or trace element versus iron correlations.

If the concentrations of trace elements in unfiltered samples are correlated with aluminum or iron, then they are most likely adsorbed to the surfaces of suspended particulates. If these correlations are linear, then the elevated concentrations are most likely natural.

3.0 Results of the Geochemical Evaluation for Multiple Elements in Soil

This section presents the results of the geochemical evaluation of arsenic, beryllium, calcium, chromium, cobalt, copper, iron, mercury, nickel, vanadium, and zinc in soil samples from Range J. Correlation plots are provided in Attachment 1.

Arsenic

As discussed in Section 2.0, arsenic has a strong affinity to adsorb on the surfaces of iron oxides in soil, so a positive correlation is expected between arsenic and iron in uncontaminated samples. A plot of arsenic versus iron is provided in Figure 1. Site surface soil samples are represented by open triangles, site subsurface soil samples by filled triangles, and background soil samples by filled circles. The plot reveals a common linear trend for the site and background samples. The site samples generally have higher arsenic concentrations than most of the background samples, but they also contain proportionally higher iron and lie on the linear trend. Arsenic in these samples is associated with iron oxides at a relatively constant ratio, and is natural.

Conclusion

Arsenic detected in the site soil samples is naturally occurring.

Beryllium

Beryllium concentrations in soil are commonly controlled through adsorption on iron oxides (Vesely, *et al.*, 2002), so a positive correlation between beryllium and iron would be expected for uncontaminated samples. A plot of beryllium versus iron is provided in Figure 2. The site and background samples form a common linear trend, and the site samples that have high beryllium concentrations also have high iron. These observations indicate a natural source for beryllium in the site samples.

Conclusion

Beryllium detected in the site soil samples is naturally occurring.

Calcium

Calcium and magnesium have similar chemical properties, and magnesium often substitutes for calcium in minerals. A plot of magnesium versus calcium is provided in Figure 3. The background samples exhibit a generally linear trend with a positive slope, and most of the site samples lie on this trend ($R^2 = 0.64$ and 0.78 for the background samples and site surface soil samples, respectively). The site samples with the highest calcium concentrations also have high proportionally higher magnesium, which indicates a natural source for the elevated calcium in the samples. There are five subsurface soil samples with low calcium that lie slightly below the background trend. The calcium concentrations in these samples are estimated ("J"-qualified) values that are well below the reporting limits; such values are highly uncertain, which may explain the low Ca/Mg ratios. These samples, however, are well below the background screening value.

Conclusion

Calcium detected in the site soil samples is naturally occurring.

Chromium

Chromium has an affinity to adsorb on iron oxides (Cornell and Schwertmann, 1996), so a positive correlation between chromium and iron is expected for uncontaminated samples. A plot of chromium versus iron reveals a collinear trend for the site and background samples (Figure 4). The site samples with high chromium concentrations contain proportionally higher iron and lie on the background trend. This indicates that chromium in these samples is associated with iron oxides at a relatively constant ratio, and is natural.

Conclusion

Chromium detected in the site soil samples is naturally occurring.

Cobalt

Manganese oxides have an affinity to adsorb divalent cations such as barium and cobalt (Kabata-Pendias, 2001). If a soil sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements. A plot of cobalt versus manganese reveals a common linear trend with a positive slope for the site and background samples (Figure 5). There are two subsurface site samples with high cobalt that lie slightly above the linear trend formed by the majority of background samples, but there are also a few background samples with similarly high Co/Mn ratios. These samples likely reflect the natural variability in Co/Mn ratios in Ft. McClellan soils. All of these observations indicate that cobalt in the site samples is associated with manganese oxides at ratios consistent with background, and is natural.

Conclusion

Cobalt detected in the site soil samples is naturally occurring.

Copper

Copper in soil has an affinity to adsorb on the surfaces of minerals such as clays and iron oxides (Kabata-Pendias, 2001). The site and background samples form a common linear trend in a plot

of copper versus iron (Figure 6). The site samples with the highest copper concentrations also exhibit proportionally higher iron, and lie on the background trend. Copper in these samples has a natural source.

Conclusion

Copper detected in the site samples is naturally occurring.

Iron

Iron oxides are minerals that are common in soil. Aluminum is a primary component of other common soil-forming minerals such as clays, feldspars, and micas. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. A plot of aluminum versus iron concentrations can be used to qualitatively assess the relative abundance of these minerals in site soil (Figure 7). The site samples exhibit higher iron concentrations than many of the background samples, but they lie on the general background trend. This indicates that iron in the site samples is naturally occurring. It is important to note that iron oxides and clays adsorb specific trace elements (as discussed in Section 2.1), so samples that plot on the upper end of the trend in Figure 7 are expected to contain proportionally higher concentrations of trace elements.

Conclusion

Iron detected in the site soil samples is naturally occurring.

Mercury

Mercury concentrations in soil are commonly controlled through organic complex formation (Kabata-Pendias, 2001), so poor correlations between mercury and iron or mercury and aluminum are often observed, even in uncontaminated soil samples. A plot of mercury versus aluminum is provided in Figure 8. All of the site samples lie on the general background trend, and the site and background samples exhibit similar correlation coefficients ($R^2 = 0.36$ and 0.34 , respectively). These observations indicate that the mercury in the site samples is associated with clays at ratios consistent with those of the background samples, and is natural.

Conclusion

Mercury detected in the site soil samples is naturally occurring.

Nickel

Nickel is commonly associated with iron oxides in soils (Kabata-Pendias, 2001). A plot of nickel versus iron reveals a generally linear trend with a positive slope for the background samples, and all of the site samples lie on this trend (Figure 9). The two site samples with the highest nickel concentrations are also characterized by high iron content, and lie on the linear trend. Nickel in the site samples is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Nickel detected in the site soil samples is naturally occurring.

Vanadium

As discussed in Section 2.1, vanadium has a strong affinity to adsorb on iron oxides in oxic soils, so a positive correlation between vanadium and iron is expected for uncontaminated samples under those conditions. A plot of vanadium versus iron reveals a strong collinear trend for the site and background samples ($R^2 = 0.99$ and 0.73 for the site surface and subsurface intervals, respectively) (Figure 10). The site samples exhibit higher vanadium concentrations than many of the background samples, but they also contain proportionally higher iron and lie on the background trend. These observations indicate that vanadium in the site samples is associated with iron oxides at a nearly constant ratio, and is natural.

Conclusion

Vanadium detected in the site soil samples is naturally occurring.

Zinc

Zinc in soil has an affinity for multiple sorptive surfaces, including clays, iron oxides, and manganese oxides (Kabata-Pendias, 2001). A plot of zinc versus iron is provided in Figure 11. The site and background samples form a common linear trend with a positive slope. The site samples with the highest zinc also contain proportionally higher iron, and lie on the trend established by the other samples. This indicates that zinc in the site samples is associated with iron oxides at a relatively constant ratio, and is natural.

Conclusion

Zinc detected in the site soil samples is naturally occurring.

4.0 Results of the Geochemical Evaluation for Magnesium and Potassium in Groundwater

This section presents the results of the geochemical evaluation of magnesium and potassium in unfiltered groundwater samples from Range J. Correlation plots are provided in Attachment 1.

Field-measured pH readings for the site groundwater samples range from 6.69 to 12.48 standard units, with a mean of 8.51, indicating neutral to alkaline conditions at the sample locations. Field-measured dissolved oxygen readings range from 0.00 to 12.75 mg/L, with a mean of 9.00 mg/L, and oxidation-reduction potential readings range from +24.3 to +426 millivolts (mV), with a mean of +241 mV. These readings suggest oxidizing conditions at most locations during the sampling event. Turbidity measurements range from 0 to 62 nephelometric turbidity units (NTU), with a mean of 8.5 NTUs. These values indicate that the site samples did not contain a significant mass of suspended particulates. It should be noted that field readings are not available for the background samples.

Magnesium

Magnesium and calcium are both major dissolved constituents in groundwater, and are derived from the weathering of silicate and carbonate minerals. A plot of magnesium versus calcium reveals a strong linear trend with a positive slope for the background samples ($R^2 = 0.91$) (Figure 12). Most of the site samples have moderately high magnesium, but they also have proportionally higher calcium and lie on the linear background trend. Magnesium in these samples is natural.

Conclusion

Magnesium detected in the site groundwater samples is naturally occurring.

Potassium

Potassium and sodium, along with magnesium and calcium, are major dissolved constituents in groundwater and are derived from the weathering of silicate minerals. A plot of potassium versus sodium reveals a generally linear trend with a positive slope for the background samples (Figure 13). Most of the site samples have moderately high potassium, but they also have proportionally higher sodium and lie on the background trend. This indicates a natural source for potassium in the site samples.

Conclusion

Potassium detected in the site groundwater samples is naturally occurring.

5.0 Summary

Geochemical evaluation indicates that detected concentrations of arsenic, beryllium, calcium, chromium, cobalt, copper, iron, mercury, nickel, vanadium, and zinc concentrations in the Range J surface and subsurface soil samples are naturally occurring. Magnesium and potassium concentrations in the Range J groundwater samples are also naturally occurring.

6.0 References

- Barclift, D., J. Heath, and A. Drucker, 2000, "Focus on Environmental Background Data Analysis," *Soil Sediment & Groundwater*, August/September, pp. 10-17.
- Bowell, R. J., 1994, "Sorption of Arsenic by Iron Oxides and Oxyhydroxides in Soils," *Applied Geochemistry*, Vol. 9, pp. 279-286.
- Brookins, D. G., 1988, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag.
- Cornell, R. M. and U. Schwertmann, 1996, *The Iron Oxides: Structure, Properties, Reactions, Occurrence, and Uses*, VCH, Weinheim.
- Daskalakis, K. D. and T. P. O'Connor, 1995, "Normalization and Elemental Sediment Contamination in the Coastal United States," *Environmental Science & Technology*, Vol. 29, No. 2, pp. 470-477.

Electric Power Research Institute (EPRI), 1984, ***Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Volume 1: A Critical Review***, EPRI EA-3356, Palo Alto, California.

Electric Power Research Institute, 1986, ***Speciation of Selenium and Arsenic in Natural Waters and Sediments, Volume 2: Arsenic Speciation***, EPRI EA-4641, Palo Alto, California.

Hem, J. D., 1985, ***Study and Interpretation of the Chemical Characteristics of Natural Water***, U. S. Geological Survey, Water Supply Paper 2254, 3rd Edition.

Kabata-Pendias, A., 2001, ***Trace Elements in Soils and Plants***, Third Edition, CRC Press.

Myers, J. and K. Thorbjornsen, 2004, "Identifying Metals Contamination in Soil: A Geochemical Approach," ***Soil & Sediment Contamination: an International Journal***, Vol. 13, No. 1 (in press).

Pourbaix, 1974, ***Atlas of Electrochemical Equilibria in Solutions***, National Association of Corrosion Engineers, Houston, Texas.

Science Applications International Corporation, 1998, ***Final Background Metals Survey Report, Fort McClellan, Anniston, Alabama***, July.

Schiff, K. and S. B. Weisberg, 1997, "Iron as a Reference Element for Determining Trace Metal Enrichment in California Coastal Shelf Sediments," in: S. Weisberg, C. Francisco, and D. Hallock, (eds.), ***Southern California Coastal Water Research Project Annual Report 1995-96***, pp. 68-78.

Stumm, W. and J. Morgan, 1996, ***Aquatic Chemistry***, Third Edition, Wiley-Interscience, New York.

U.S. Environmental Protection Agency, 1995, ***Determination of Background Concentrations of Inorganics in Soils and Sediments at Hazardous Waste Sites***, Office of Research and Development, EPA/540/S-96/500, December.

U.S. Navy, 2002, ***Guidance for Environmental Background Analysis, Volume 1: Soil***, NFESC User's Guide UG-2049-ENV, Naval Facilities Engineering Command, Washington, D.C., April.

Vesely, J., S. A. Norton, P. Skrivan, V. Majer, P. Kram, T. Navratil, and J. M. Kaste, 2002, "Environmental Chemistry of Beryllium," in: Grew, E. S. (ed.), ***Reviews in Mineralogy and Geochemistry, Volume 50, Beryllium: Mineralogy, Petrology, and Geochemistry***, Mineralogical Society of America, Washington, D.C.

ATTACHMENT 1

